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Future-competing battery chemistries for large-scale energy storage

Alternatives to be used instead of lithium-ion in the coming 5-10 years

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Abstract

With net-zero emissions set to be achieved in the EU by 2050, the transition from fossil-based energy sources to more renewable and green options are ever expanding. This puts a strain on the electricity grids because of the intermittent nature from these energy sources. To mitigate this battery systems are used, of which the lithium-ion battery is the most prevalent, and expected to only increase in use. However, material resource concerns and possible danger of over-reliance on one technology has opened up for a search to find other alternatives that could be used instead or in conjunction with the battery. Out of a long list of batteries, the nickel-hydrogen battery, zinc-bromide flow battery and iron-air battery are three alternatives that have been identified to have potential. Their suitability was researched and discussed for various grid-applications. The result of which showed that out of the three, it is only believed that the nickel-hydrogen battery have a definitive competitiveness, that the zinc-bromide flow battery has few things going for it, and that the iron-air battery has large potential but just as large uncertainty surrounding its future. Lastly, a specific off-shore wind park case was investigated to see the practicality and competitiveness of the nickel-hydrogen battery compared to a specific lithium-ion chemistry.

Keywords

Battery energy storage systems, Nickel-hydrogen battery, Zinc-bromide flow battery, Iron-air battery, Large-scale applications

Sammanfattning

'Netto-noll utsläpp' i EU vid 2050 är en av målen för att påskynda övergången från fossila bränslen till mer förnyelsebara och hållbara alternativ. Detta har däremot introducerat mer turbulens på elnäten. Ett av verktygen för att reglera och förbättra eldistributionen är stor-skaliga batterier, där litium-jon är den mest förekommande kemin. Men på grund av oro kring resursutbud och hopp om teknologi diversifiering har det påbörjat en sökning efter alternativ som kan användas istället eller tillsammans med litium-jon batterier. Från en lång lista så har tre alternativ med hög potential identifierats. Vilket inkluderar, nickel-vätgas batteri, zink brom flödes batteri och järn-luft batteri. Deras lämplighet undersöktes och diskuterades för flertalet användningsområden och för ett speciellt case av Vattenfall. Slutsatsen var att utav de tre, så är det endast nickel-vätgas som kan förväntas vara ett bra alternativ för specifika fall, att zink-brom har få möjligheter att konkurrera och att järn-luft har väldigt hög potential men också många oklarheter som gör det svårt att förutspå dess utveckling.

Nyckelord

Batteri energilagringssystem, Nickel-vätgas batteri, Zink brom flödes batteri, Järn-luft batteri, Storskaliga användningsområden

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List of acronyms and abbreviations

aFRR	Automatic Frequency Restoration Reserve
BESS	Battery Energy Storage System
BTM	Behind The Meter
CAPEX	Capital Expenditure
CED	Cumulative Energy Demand
DoD	Depth Of Discharge
DSO	Distribution System Operator
FCR	Frequency Containment Reserve
FCR-D	Frequency Containment Reserve Down
FCR-N	Frequency Containment Reserve Normal
FCR-U	Frequency Containment Reserve Up
FeOB	Iron-Air Battery
FFR	Fast Frequency Reserve
FSP	Flexibility Service Provider
FTM	in-Front of The Meter
GWP	Global Warming Potential
HER	Hydrogen Evolution Reaction
HOR	Hydrogen Oxidation Reaction
HVAC	Heating, Ventilation and Air Conditioning
LCOS	Levelised Cost of Storage
LFP	Lithium Iron Phosphate
LIB	Lithium-Ion Battery
mFRR	Manual Frequency Restoration Reserve
NaIB	Sodium Ion Battery
NaSB	Sodium Sulphur Battery
NiHB	Nickel-Hydrogen Battery
NMC	Nickel Manganese Cobalt lithium battery

OER	Oxygen Evolution Reaction
OPEX	Operational Expenditure
ORR	Oxygen Reduction Reaction
RFB	Redox Flow Battery
RTE	Round-Trip Efficiency
SoC	State Of Charge
SOFC	Solid-Oxide Fuel Cell
SOMARB	Solid-Oxide Metal-Air Redox Battery
TRL	Technology Readiness Level
TSO	Transmission System Operator
VRFB	Vanadium Redox Flow Battery
ZBFB	Zinc Bromine Flow Battery

Chapter 1

Introduction

With net-zero emissions set to be achieved in the EU by 2050 [1], the current transition from fossil-based energy sources to renewable energy is ever expanding, more and more countries turn to green energy such as photovoltaic or wind power. However, most renewable energy sources are variable in their nature, meaning that they cannot provide reliable power whenever asked. This is because their power output is dependent on climate and weather, such as solar power not being possible without any irradiation. This intermittency then puts strain on the electricity grid. To mitigate this, the interest in energy storage has increased, to store excess power for later when the climate is not as favourable or to equalise power output to help the electricity grid.

In 2021, the total global installed capacity for energy storage amounted to 160 GW, most of the capacity in the form of pumped-hydro storage. Although, the technology is geographically-dependent and therefore not applicable at every location. Interest for other more scalable alternatives, such as **Battery Energy Storage System (BESS)** has therefore increased, pushed by a large cost reduction. In 2021, only 10% of global installed capacity was grid-scale **BESS**. However, the installations compared to the previous year had increased by 60% and is expected to continue doing so. [2]

The large share of newly built battery capacity consists of **Lithium-Ion Battery (LIB)**s, which is the most common battery type used for any chemical energy storage today. This is because of their high energy density, long lifespan, and low self-discharge [3]. However, **LIBs** face struggles such as fire safety and recycling, both of which is even more challenging for larger scales [4]. Recycling especially being increasingly important as lithium is a scarce resource, which utilisation is expected to grow as the transport sector is set to primarily utilise **LIBs** when transitioning from fossil-powered propulsion. For

instance, it is estimated that lithium in circulation will grow 30-times til 2030 compared to ten years earlier, and by 2050 it will have increased a 100-fold [5].

Because of the increasing usage and an already strained lithium production, searching for alternative battery technologies that can be used instead of LIBs in large-scale is important. Today there is a plethora of available alternatives, that is either already fully commercialised, about to be, or still in an early development phase. Therefore, the aim of this thesis is to investigate a range of alternative non-lithium-based battery chemistries that has the potential to replace LIBs in identified use-cases where that could be possible.

Important to note is that this thesis is written together with Vattenfall AB, one of Europe's largest producers and retailer of heat and electricity [6]. The company is originally from Sweden, and is completely owned by the Swedish state.

1.1 Aim and Objectives

The aim of this report is to perform a literature review and identify 2-3 up-and-coming battery chemistries that have the potential to be used for large-scale energy storage application and evaluate them in comparison to the LIB. To involve stakeholders, manufacturers and suppliers in the discussion

In contrast, the objective of this thesis is to spread and increase knowledge of the wide arrange of other batteries capable to be used as large scale energy storage.

1.2 Research Questions

The research questions that are chosen to reflect the aim of the thesis are selected to help create a transparent red thread throughout the report. These questions are the following:

1. What battery chemistries in the next 5-10 years are available and suitable for grid-scale energy storage application?
2. Which 2-3 batteries show most promise for selected criterion?
3. How well are the selected batteries suited for various applications and services, and how do they compare to the LIB for the same case? Are

they a transition technology or a long-term technology either with or without improvements?

4. For a specific case provided by Vattenfall, how does the selected batteries perform and are they preferred over a **LIB**?

1.3 Delimitations

To begin, the focus is on large-scale applications with stationary operation, which means performing a charge/discharge cycle in a fixed geographic location. Furthermore, as the aim of this thesis is to look at what batteries that will be suitable and able to be used in the coming 5-10 years, this means that it requires a technology to be at a stage where they have already been largely proven or are ready to be commercialised. This will be quantified by **Technology Readiness Level (TRL)**, where it is expected that the batteries should have achieved TRL 6-7 by the end of 2023. This will be further explained later in the Chapter 3 - Methodology. Another part is that since the aim is to investigate alternative batteries to **LIB**, technologies that are at the same **TRL** as it will not be explored in more detail. This is for two reasons: (1) As the aim is on alternative batteries, this puts emphasis on finding technologies that are not already as commercialised as the **LIB** is and (2) that Vattenfall have already performed a study investigating some battery chemistries that are close to commercialisation. Therefore, this work aims to expand on that list. Furthermore, the use-cases which are investigated will be limited, and feature predominantly grid-applications. Lastly, sustainability and environmental impact are wide topics with many nuances. In this work when discussing sustainability, it will primarily refer to resource availability and supply stability while environmental impacts will be limited to **Global Warming Potential (GWP)** and **Cumulative Energy Demand (CED)** during production. Other issues and questions are left out for simplicity.

Chapter 2

Background

2.1 Key Concepts

2.1.1 Energy Storage Fundamentals

The concepts that will be used to evaluate and discuss the batteries brought up in this work are presented below.

Energy density – energy capacity per volume or litre, therefore presented as Wh/L.

Specific energy – a technology's capacity to store energy per unit of mass, presented as Wh/kg.

Specific power – a technology's capacity to deliver power per unit of mass, presented as W/kg.

Capacity – how much specific energy that can be stored, represented as in ampere-hours (Ah).

C-rate – how quickly a battery is charged or discharge, where the convention is that at 1C the battery rate is the same to its marked Ah rating. This means that if a fully charged battery that is rated as 1 Ah is operated at 1C, then it will last 1 hour, and for 0.5C or 2C it is double or half the duration respectively. [7]

Cycle life – The amount of complete cycles of charge and discharge a battery can perform. This is heavily dependent on how the battery is operated and under what conditions. [8]

Calender life – The life time of a battery. More common to use this parameter than cycle life for batteries that are only cycled few times at most. However, neither parameter is exclusive to each other. [8]

State Of Charge (SoC) – a parameter that refers to the available capacity

of the battery at specific time [9], often as a percentage. It is calculated as Eq. 2.1, where C is the time specific capacity, while C_0 is the capacity available when fully charged.

$$SoC = \frac{C}{C_0} \quad (2.1)$$

Depth Of Discharge (DoD) – how much of a battery’s stored capacity that is utilised during discharge [10]. Its the opposite of **SoC** and therefore can be calculated as Eq.2.2.

$$DoD = 1 - SoC = 1 - \frac{C}{C_0} \quad (2.2)$$

Self-discharge rate – the phenomena of loss in stored energy from internal processes that reduces the stored energy over time. Caused by things such as friction, leakage, side reactions or resistances. Often presented as a percentage of lost capacity over a time-period such as a day or hour. [11]

Response time – The time for a system to reach its full output, or nominal power after being idle or on standby [11]. Different applications have different requirements. The

Round-Trip Efficiency (RTE) – is the percentage of the stored energy that is later retrieved after storage [12], meaning that its a ratio between the energy output and energy input from and to the system respectively. No system can achieve a 100% efficiency, as there is always some resistances. The usual range for developed batteries is between 70-95% [13].

2.1.2 Battery Risks

Independent of cell chemistry and use-case, according to Brandt *et al.*, there are four categories that the risks of a battery in general fall into: (1) thermal, (2) chemical, (3) electrical and (4) kinetic [14]. Even if separated into various categories, many events and risks are interconnected, meaning one can increase the potential of the other.

The first one is thermal which comes from batteries being very energy dense, meaning that if the energy is released in an uncontrolled way there will be a large emission of heat, which in turn makes the temperature of the cell increase to dangerous levels. Reasons for this could be an external or internal error, such as overcharge or voltage reversal and external heating. Another danger is thermal runaway, as new chemical reactions could take place at an elevated temperature, which in turn releases heat further increasing the chance of exothermic reactions and in doing so creating a feedback loop. This is

less common for small batteries, but since larger batteries have a lower ratio of surface area to volume, this then means that less heat is transferred to its surroundings and a higher thermal concentration is possible. A way to mitigate this is by ventilation or cooling systems, although at the expense of the system efficiency.

The second is chemical, when some kind of reaction taking place that increases the risk of or creates a dangerous event. This includes things such as leakage of a flammable liquid electrolyte, toxic gas formation from either interaction between cell compounds and external air, or caused by elevated temperature opening up for dangerous side-reactions. This is usually triggered by manufacturing defects or cracks in the shell caused by external effects. A safety check before use therefore a good way to avoid this issue.

Third is electrical risks. In contrast to power supplied by the electricity grid, which can be turned off, batteries cannot be completely switched off. Even if the battery is completely discharged, it will still have voltage close to its designed value and is capable to produce significant current. For large scale batteries, this is even more of a risk as the voltages are much higher. Correct safety measures to keep untrained personnel from exposed areas is therefore a good idea.

Fourth and last category of risk is kinetically. This refers to the unfortunate case when there is system failure (*e.g.*, a thermal runaway happening or cell failure), of which there is then a chance that cell parts could be sent flying and/or a blast wave is produced. It is therefore a good idea not to place a system where this is possible close to civilians or important infrastructure.

2.1.3 System Cost

No matter the impressive performance and characteristics of a technology if its cost is not competitive it will not see wide-spread commercial success. Therefore, it is key to figure out what the cost of a **BESS** is to make proper comparisons. Sadly, there is not a straightforward answer to this, as depending on use-case and question asked or what it is compared to, there will be different answers [15]. The most simple parameters is cost per kilowatt or per kilowatt-hour. However, these two parameters is not easily comparable between different systems and technologies.

It is therefore difficult to have a single parameter fit for all cases. The believed best alternative for **BESS** is to calculate the **Levelised Cost of Storage (LCOS)**, which quantifies the discounted cost per unit of discharged electricity for a specific storage technology and application (meaning cost/Wh) [16]. The

LCOS can be calculated by Equation (2.3), based on the work by Julch *et al.*, [17], where **Capital Expenditure (CAPEX)** is the initial investments, W_{out} which is the sum of energy output over the lifetime n , A_t which is the total annual costs and maintenance, the discount rate i to compensate for the loss of value in money over time, and t which is a specific time.

$$LCOS = \frac{CAPEX + \sum_{t=1}^{t=n} \frac{A_t}{(1+i)^t}}{\sum_{t=1}^{t=n} \frac{W_{out}}{(1+i)^t}} \quad (2.3)$$

The annual cost and maintenance, A_t , is calculated by Equation (2.4), where **Operational Expenditure (OPEX)** is the maintenance performed and $CAPEX_{re,t}$, which is the potentially necessary capital replacement for that year, the cost of electricity c_{el} , the total input of electricity W_{in} at time t , and R_t , the recovery value of the system at time t .

$$A_t = OPEX + CAPEX_{re,t} + c_{el}W_{in} - R_t \quad (2.4)$$

Lastly, the total input of electricity, $W_{in,t}$, can be calculated by Equation 2.5, where η_{RTE} is the **RTE**, the self-discharge rate, r_{sd} , the rated capacity, C_r , and the duration energy is stored per year, T .

$$W_{in_t} = \frac{W_{out,t}}{\eta_{RTE}} + TC_r r_{sd} \quad (2.5)$$

2.1.4 Technology Readiness Level

A common tool to evaluate at what stage of development or commercialisation a technology is at is by the **TRL**. It is usually a list of criteria for specific levels that has to be met for a technology to be classified as such. The European commission has made their own list and respective criteria per stage that must be filled for a technology to be considered at that level. This is presented in Table 2.1.

Table 2.1: European Commission’s list and criteria for technology readiness levels [18].

TRL 1	Basic principles observed
TRL 2	Technology concept formulated
TRL 3	Experimental proof of concept
TRL 4	Technology validated in lab
TRL 5	Technology validated in relevant environment (industrially relevant in the case of key enabling technologies)
TRL 6	Technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
TRL 7	System prototype demonstration in operational environment
TRL 8	System complete and qualified
TRL 9	Actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or space)

2.2 Large-scale Energy Storage Applications

In energy storage systems it is common to classify a use-case as either **in-Front of The Meter (FTM)** or **Behind The Meter (BTM)**. **FTM** batteries are connected to a larger distribution grid to alleviate system irregularities, perform frequency control, generation etc. **BTM** batteries on the other hand are connected to a local system who is in turn connected to the larger electricity grid through an utility meter, therefore “behind-the-meter”. A common reason for using **BTM** batteries is for electricity bill savings. [19]

Table 2.2: List of described use-cases and whether they are in front-of-the meter (FTM) or behind-the-meter (BTM)

Load-Frequency Control Services	FTM
Voltage Control	FTM
Congestion Management	FTM
Black Start	FTM
Backup Power	BTM
Peak Shaving	BTM
Energy Arbitrage	BTM
Renewable Integration	FTM
Local Flex Markets	BTM

2.2.1 Load-Frequency Control Services

One of the most important factors to keep consistent in an electrical grid is the frequency. If there is more power generation than consumption in the grid, or the reverse, then the frequency will decrease or increase respectively. If the frequency deviates too much, then the grid becomes unstable, increasing the danger of emergency shut down. Luckily, there is some inertia against fluctuations, by the inherent mechanical properties of the synchronous generators who generate the frequency in the grid by either speeding up or slowing down to reduce it. Although, when that is not enough other control services are activated. [20]

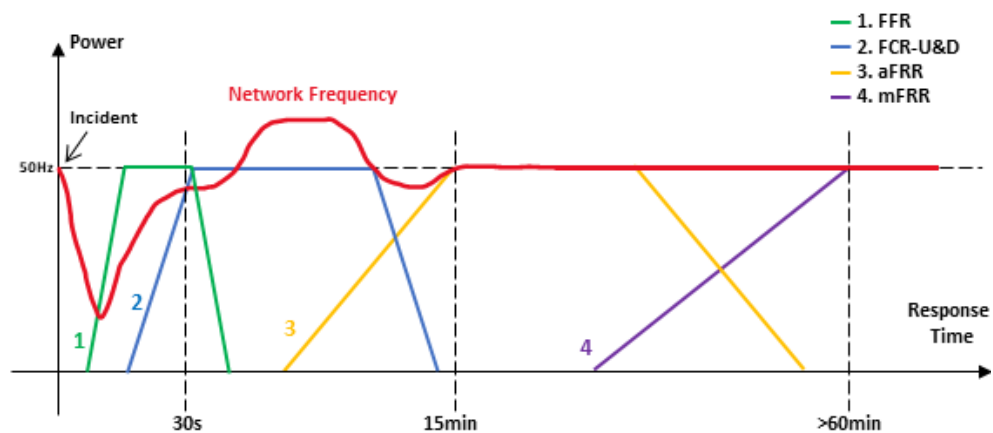


Figure 2.1: Time frame of operational frequency control services in the Swedish grid. Not to scale.

In Sweden the nominal frequency is 50 Hz, and should of course be as stable as possible. Out of the control services that are used, the first one to be activated is **Fast Frequency Reserve (FFR)**, which is used to counteract the initial quick and deep frequency deviations [21]. This is then followed by **Frequency Containment Reserve (FCR)**, which is automatically triggered to bring the grid to a steady state value by either generation or consumption of power to the grid [20]. In Sweden this is split into three types. Either an "up" or "down" service called **Frequency Containment Reserve Up (FCR-U)** and **Frequency Containment Reserve Down (FCR-D)** respectively, and one that does both called **Frequency Containment Reserve Normal (FCR-N)** [22]. Afterwards, other services are then activated to then fine-tune the grid frequency to its nominal value. This includes **Automatic Frequency Restoration Reserve (aFRR)** and **Manual Frequency Restoration Reserve (mFRR)** of which the difference is only that one is automatic and the

other is by a request from Svenska Kraftnät. A schematic diagram shows the relationship between the frequency and each control service in Figure 2.1. All of the aforementioned load-control services can be performed by a BESS [20], however for the analysis, mFRR will not be included, as it is not expected that any battery at the moment will be used for it.

The various qualifications of requirements for each service demanded by the Svenska Kraftnät can be viewed in Table 2.3.

Table 2.3: Overview of the requirements for Frequency control services stipulated by Svenska Kraftnät [22]

Type	FFR	FCR-U&D	FCR-N	aFRR	mFRR
Minimum size	0.1MW	0.1MW	0.1MW	1MW	10MW (5MW at SE4)
Activation Requirement	Automatically when deviations in frequency	Automatic linear activation within range: 49.90-49.50Hz or 50.10-50.50Hz	Automatic linear activation within range: 49.90-50.10Hz	Automatically at deviations from 50.00Hz	Manual request from SVK
Activation Time	Three alternatives for 100%: 0.7s at 49.5Hz 1.0s at 49.6Hz 1.3s at 49.7Hz	50% in 5s or 100% in 30s	63% in 60s or 100% in 3min	100% in 5min	100% in 15 min
Demand SVK	Up to ~100MW	Up to 558MW	231MW	Up to 111MW	No specified requirements
Duration	30s or 5s	at least 20min	1 hour	1 hour	1 hour

2.2.2 Voltage Control

In the electricity grid, different voltage levels are used to efficiently transfer electricity. Therefore, unlike frequency which is sought to be kept constant over the total system, voltage varies depending on the location. Two important concepts with regard to voltage control is active and reactive power. Active power is the power that is ‘actually’ used in an electric circuit, while reactive power continuously flows between load and source [23]. The voltage level in a grid depends on the relationship between these two and could therefore be controlled by adjusting any of the two. For high voltage transmission lines, it is common to adjust only reactive power as there are less active-power losses at high voltage, while in distribution grids both are adjusted at the same time because of the lower voltage. BESS are perfectly suited for voltage control as they are capable of injecting both active and reactive power. Therefore, a BESS is a great choice for voltage control in any parts of the grid. [20]

For a system to perform voltage control, a capacity of a few MW up to a hundred is required [24, 25]. It should also have a minimum response time

around a millisecond, and be able to discharge for a couple minutes [24]. The discharge is done in up to 5 pulses in sequence, 10 seconds each, although only expected to be needed once a month [25].

Table 2.4: Technical requirements for voltage control

Size (MW)	1-100
Response Time	ms
Discharge Duration	1-5min
Cycles per year	12

2.2.3 Congestion Management / Local Flex Markets

Even though an electricity grid cannot physically be congested, the term refers to the more complex situation of whenever active power transfer from the transmission grid exceeds its capability [26]. There are two ways to solve congestion: to limit the power transfer or to increase the capacity of the transmission grid [20]. However, neither option is optimal, as the first option would impact users of the grid negatively, while the second is neither time- nor cost-effective. Instead, an alternative is to use energy storage to manage active power at the congestion point, ensuring a stable throughput of power from its own storage [20]. Using a BESS would be a cheaper way to limit congestion in the grid, as the whole grid would not have to be improved. The requirements for such a system can be hard to generalise, as it varies a lot. What is expected though, is that the discharge duration should be around 1-4 hours, and that 50-100 cycles per year is probably performed [27]. Furthermore, the size range for this application is stated to be between 1-100 MW.

Table 2.5: Technical requirements for congestion management

Size (MW)	1-100
Discharge Duration	1-4 hours
Cycles per year	50-100

There are also other ways to mitigate congestion. The initiative CoordiNet as part of the Horizon 2020 program by the EU Commission, is a project to achieve flexible electricity markets by increasing the coordination between the Transmission System Operator (TSO) and the Distribution System Operator (DSO) [28]. In the project, various demos have been performed, of which some have taken place in Sweden where Vattenfall have participated, as well

as in a standalone project in Stockholm called sthlmflex [29]. The basic idea is to allow for flexible agents (consumers or providers and end-users), to increase or decrease their demand or generation as needed to stabilise the grid [28]. In the programme they are called **Flexibility Service Provider (FSP)**, and because they provide a service they are compensated monetarily for it. Often, revenue created by these actors are directly linked to their consumption or generation of electricity. Therefore, a way to allow them to both be flexible with consumption/generation but also a consistent operation, would be by introducing a **BESS**. This way, energy can be stored and provided as necessary instead of change to operation.

The technical requirements varies depending on project. In the CoordiNet project, Vattenfall did two congestion management projects [30]. The first one for a dayahead market with a quote size of at minimum 0.1MW and an endurance of 60 minutes. The second was a peer to peer market (meaning producer or consumer market, independent of the **DSO**), that had a quote size of at minimum 1MW and an endurance of 60 minutes. Standalone **BESS** used in the project was one in Uppland with 5MW/20MWh and Skåne with 0.45MW/1MWh [31]. The Skåne battery was only called twice and once for the winter period 21/22 and 22/23 respectively, for a total of 5 hours, otherwise it was on standby [32].

Similarly, in sthlmflex, an **FSP** should be able to decrease or increase their demand/generation at minimum 0.1MW for an hour [33]. The peak hours where this is needed is 07.00-11.00 and 15.00-21.00, and up to 160 hours was available for provision before the winter season 22/23.

Table 2.6: Technical requirements for local flex markets.

Size (MW)	0.1-5
Discharge Duration	1-4 hour
Cycles per year	few
Storage duration	long/unknown

2.2.4 Black Start / Backup Power

Black start refers to the process in which the electrical grid or parts of it is restored to operation without relying on an external transmission network [20]. This cannot be achieved by traditional generation units as they lack the capability. This has instead been achieved by smaller units such as fossil-fuelled generators. Lately it has been investigated if **BESS** could instead

provide this function, which was shown to be possible in 2017 [34]. Still, **BESS** is a recently discovered alternative and have yet to reach wider use – but could very well do so in the future as fossil-fuelled alternatives are phased out [20].

The technical specifications required for black start is that the systems size is in the range of 5-50 MW, can handle discharge duration of 15 minutes to an hour, and capability to perform at minimum 10-20 cycles per year [27]. The **BESS** must also be capable of deep **DoD** and have a high mean **SoC** [35].

Table 2.7: Technical requirements for black start. DoD = Depth of Discharge, SoC = State of Charge

Size (MW)	5-100
Discharge Duration	15min-1hr
Cycles per year	10-20
DoD	deep
SoC	high

Similar to black start is backup power which is when an energy storage is used in cases when there is a blackout. The difference from black start is that it does not target the grid, instead it provides power to a single demand or service that can't lose power because of security or safety reasons [36]. This includes examples such as hospitals, airlines computers or state defence electronics. Because it has life affecting consequences, there are some strict requirements a **BESS** needs to meet. This includes a quick response time as well as quickly reaching 100% efficiency without any interruptions or large deviations during operation. The **BESS** should also be capable of several hours of discharge. The amount of cycles per year needed depends on placement, as certain regions are more vulnerable to black outs.

Table 2.8: Technical requirements for backup power.

Size (MW)	specific
Response Time	ms
Activation Time	instant
Discharge Duration	hours
Cycles per year	unknown

2.2.5 Peak Shaving

When consumers (either commercial or industrial) use electricity, they do not only pay for the energy they use, but also a peak demand charge, which is proportional to their highest measured consumption over a certain time-period (conventionally a month or a year). Therefore, peak shaving refers to minimising that peak consumption in an effort to save money, which can be done by storing cheap energy in a **BESS** and utilising it during peak demand periods. This is especially useful for power intensive industries who want to operate during daytime since that is when their workers are available. Moreover, less strain is put on the transmission grid while also saving the consumer money. [20]

The usual requirements for a peak shaving system is that it should have a capacity between 0.25-25 MWh and power capability of 0.05-5 MW as well be able to perform 300-400 cycles per year [35]. The usual discharge duration is between 1-6 hours [27].

Table 2.9: Technical requirements for peak shaving.

Demand (MW)	0.05-5
Capacity (MWh)	0.25-25
Discharge Duration	1-6hrs
Cycles per year	300-400

2.2.6 Energy Arbitrage

Somewhat the opposite of peak shaving, energy arbitrage (sometimes called time-shifting in literature) entails storing energy whenever it is cheap, and then selling it at time-periods when the price of electricity is high – therefore creating profit. In Sweden, the electricity price works on a day-ahead system, meaning that the price of electricity is set 24 hours before [37]. The highest price is usually around 07:00 in the morning and 18:00 in the afternoon, while it is the cheapest shortly after midnight [38]. A **BESS** is very much usable for this application.

Since there is a daily loop of when the price is usually cheapest and most expensive, a **BESS** only employed for energy arbitrage can be expected to have 1 cycle per day and does not require a large capacity as its storage time will at most probably be about between 5-6 hours [39]. Furthermore, a benefit is if the system has a quick charge and discharge rate. Although, the usual discharge duration is around 3-12 hours [24]. Moreover, a quick response rate

is beneficial but not necessary. Lastly, an influential parameter is **RTE**, as a decrease in efficiency is a direct loss in profit which for this application is especially an important parameter [39].

Table 2.10: Technical requirements for energy arbitrage.

Response Time	ms
Discharge Duration	3-12hrs
Cycles per year	365
RTE	High

2.2.7 Renewable Integration

Instead of solving issues in the grid, utilising a **BESS** directly at the source of power generation is a way to regulate power dispatch to the grid. This is especially good for renewable power systems, whose power delivery can fluctuate rapidly. A **BESS** is very much suited for this since they have quick response time and the ability to deal with high levels of fluctuations. This allows for more flexibility in scale of deployment for renewable power generation.

The technical requirements for this application is highly dependent on the renewable power system. A solar plant for example operate only when the sun is out which is only once for generally half a day, while a wind-power plant can operate whenever there is enough wind, which can vary a lot during a day or longer period. Furthermore, because of their difference, energy storage is most often used differently depending on source. For solar power, since its power output is very cyclic and matches demand quite well over a day, a integrated **BESS** often perform capacity firming for it, which means making an intermittent power source more stable by the inclusion of a storage system to stabilise power output. This is also done for wind power, but because of the more rapid change in power output and generation over a whole day, a storage system could also be used to do energy arbitrage, to make profit from the power generation during night when demand is low. [39]

In this work it will be assumed that the same technical requirements will be used for renewable energy arbitrage as non-renewable arbitrage. In the case of capacity firming, it varies slightly between solar- and wind power. For solar, a discharge duration of 1-2 hours will be assumed, while wind is a bit longer with 2-3 hours. Moreover, it is very important that the discharge is "firm", otherwise large financial penalties will follow [39]. Furthermore, the size is

highly specific for each generation type, and varies from case to case. For example, solar generation could decrease because of cloud cover for just an instant or longer, and how much is lost in power from the rated level depends.

Table 2.11: Technical requirements for renewable capacity firming.

Requirement	Solar	Wind
Discharge Duration (hrs)	1-2	2-3
Cycles per year	365	365+

2.3 Electrochemical Energy Storage Technologies

There are plethora of batteries available today, too many to name them all. A selection of them are presented in this section, detailing their principle, materials, performance, and applications. A quick summary of them and their respective advantages and disadvantages are collected in Table 2.12.

Table 2.12: Summary of the advantages and disadvantages of each battery studied.

Battery	Advantage	Disadvantage
Lithium-ion	<ul style="list-style-type: none"> - High-specific energy - Low Self-discharge - High efficiency 	<ul style="list-style-type: none"> - Non-abundant material - High risk of thermal-runaway
Vanadium Redox Flow	<ul style="list-style-type: none"> - Easily scalable - High cyclelife - Can be recharged by replacing electrolyte 	<ul style="list-style-type: none"> - Expensive and scarce material - Low energy and power density
Sodium Sulphur	<ul style="list-style-type: none"> - High energy and power density - High Efficiency 	<ul style="list-style-type: none"> - High operation temperature - High self-discharge
Sodium-Ion	<ul style="list-style-type: none"> - Possess similar qualities to lithium-ion - More abundant and cheap material 	<ul style="list-style-type: none"> - Mostly worse performance than lithium-ion
Nickel-Hydrogen	<ul style="list-style-type: none"> - Very high cycle life and durability - Low maintenance 	<ul style="list-style-type: none"> - Pressurised cell - High self-discharge
Zinc-Bromide Flow	<ul style="list-style-type: none"> - High DoD capability - Theoretically endless lifetime 	<ul style="list-style-type: none"> - Needs to be fully discharged each week - High cost of power
Iron-Air	<ul style="list-style-type: none"> - Up to and over 100hrs discharge - Safe and abundant material 	<ul style="list-style-type: none"> - Largely unexplored - Low efficiency
Solid-Oxide Metal-Air	<ul style="list-style-type: none"> - High performance in lab-size 	<ul style="list-style-type: none"> - Early concept and underdeveloped

2.3.1 Lithium-ion Batteries

As mentioned in the introduction, **LIBs** are the current market standard for almost every battery storage. This is because of their long-life cycle, high operating voltage, and low self-discharge rate, and more [40].

Overview of the Technology

A **LIB** is made up of two electrodes (anode and cathode), a separator, an electrolyte and two current collectors. The electrolyte carries the charged lithium-ions between the two electrodes back and forth depending on operation. This creates free electrons at either the anode or cathode depending on if its charged or discharged respectively. Because the separator does not allow electrons to flow through it, they are instead forced to go through the current collectors instead (who are connected to a load), therefore creating current. [41]

For grid-scale **BESS**, individual cells must be put together to be able to generate the voltage needed. The individual cells can be made into various forms, but for **LIBs** used in large scale, the cylindrical and prismatic design is most commonly used.

Performance and characteristics

There are many different **LIB** chemistries that are in use today. Two of the most common are discussed in this work, which are **Lithium Iron Phosphate (LFP)** and **Nickel Manganese Cobalt lithium battery (NMC)** [42]. The various performances and characteristics of the two chemistries are presented in Table 2.13. As can be observed, the two have different strengths and weaknesses. In general though, the key strengths of **LIBs** are their high specific energy and intermediate specific power coupled with high voltage. Most chemistries also have pretty good cycle life and with a self-discharge much lower than most batteries [24]. For economics, the **LIB** has seen great reductions in its cost as of recently. Last year, the capital cost of energy and power was 33-250\$/kWh and 265-358 \$/kW [43].

Table 2.13: Comparison of the two lithium-ion chemistries. [42].

Chemistry	LFP	NMC
Specific Energy (Wh/kg)	90-120	150-280
Energy Density (Wh/L)	190-300	325
Specific Power (W/kg)	4000	1000-4000
Power Density (W/L)	10k	2k-10k
Cell Voltage	3.3V	3.7V
Cycle Life	5k-6k	3k-4k
Self-discharge (% per month)	<1%	1%
Operating temperature	-20° to +60°	-20° to +55°

Materials

Traditionally, materials that are used in a **LIB** is lithium metal oxide for the cathode, graphitic carbon as the anode, and inorganic dissolved lithium salts

as the electrolyte [44]. Some of the commonly used materials are causing concerns, especially as demand grows for LIBs.

The first one to discuss is lithium itself. It is the lightest metal, and has some unique properties compared to other alkali-metals, which give rise to its high versatility and why it's hard to replace [45]. For instance, it has the highest electronegativity while also the smallest ionic radius for the alkali-group. Although great advantages, there are still problematic questions surrounding its availability. Currently, 22% of the global lithium demand is accounted for by the battery market [46], and 43700 tonnes of lithium per year is consumed by batteries alone [45], which is only expected to grow. In 2017, the European commission assessed lithium to be on the threshold to be in supply risk, and three years later in 2020, it finally got onto the list of critical raw materials [45]. What makes things worse is that there is clear discrepancies between sources and contradicting information how much lithium that is available and whether it will be possible to scale up production enough to meet the growing demand [46, 47]. It is therefore important to reflect for what the available lithium should be used for.

Cobalt is one of the key cathode materials in use today, used in various LIB chemistries such as the NMC. Even though it is widely used, manufacturers are trying to reduce the amount of cobalt consumed, partly because of its large cost and sustainability concerns. The other part is that about half of global production of cobalt is used for secondary batteries. As a rare earth metal, its abundance is low and increasing production could prove difficult. The majority of it is also mined in one geographic region – the Democratic Republic of Congo, which is not ideal. There are also reported instances of illegal working conditions, such as child labour, during the extraction of the metal in Congo. [48]

Another cathode material is phosphate, used by the LFP chemistry. With it, the chemistry demonstrates better tolerance to full charge conditions and experiences less strain from prolonged operation at high voltage in contrast to other lithium-ion systems. However, the trade off is a lower nominal voltage and higher self-discharge, at least when compared to the NMC. It is also important to ensure cleanliness during production as moisture can heavily affect the lifetime. [49]

Moving on to the anode, the most dominant material currently is graphite, which is a form of elemental carbon. Even though it is named after lithium, in a LIB there is actually more graphite than lithium. Some claim a ratio as high as 1:5. One of the most important characteristics of this material is its purity. The three natural kinds of graphite; flake, amorphous and vein are used

depending on the criteria of quality. The most abundant kind, amorphous graphite, is not at all used in LIBs. Instead, what is most commonly used is flake-graphite, which even though less pure than vein, has a lower cost because of its abundance. On top of natural graphite, there is synthetic graphite. The natural kind has a highly crystalline structure while the synthetic kind less so and therefore has a worse electrical and thermal performance. It has also been more expensive historically because of difficult production. However, synthetic graphite can be tailored made to have specific performance characteristics which gives them a competitive edge. The global reserves of carbon are more evenly spread out than cobalt, still most of the mineral is found concentrated in places such as Turkey, Brazil, and China. It is expected that existing reserves will last a bit longer than 200 years, but only if demand stays constant – which is unlikely. [48]

Sustainability, Environmental, Safety and Ethical concerns

When it comes to sustainability, Peters *et al.*, made a review of life-cycle-analysis studies performed on LIBs [50]. It was shown that on average, for each Wh produced, it meant a cumulative energy demand of 328 Wh and caused 110 gCO₂-eq in greenhouse gases. This was also broken down for each chemistry and is shown in Table 2.14.

Table 2.14: Mean-value of the respective impact category for the two lithium-ion chemistries. CED = Cumulative Energy Demand and GWP = Global Warming Potential [50]

	CED	GWP
	[MJ/Wh]	[(kgCO ₂ -eq)/Wh]
LFP	0.97	0.161
NMC	1.03	0.160

A large challenge for large scale utilisation of LIBs is safety, especially fire-safety. The operating thermal range of LIBs is, as can be observed in Table 2.13, around -20°C to +60°C depending on chemistry. Since it is in the range of ambient temperature, it is therefore susceptible to its environments for its operation temperature which increases the need for ventilation or other methods. Moreover, the capacity of a battery is related to the operating temperature, where it degrades quicker if temperature is higher. More importantly, if operated at elevated temperatures outside its design, the LIB is susceptible for thermal runaway, especially when compared to other batteries. [51]

Another problem is transport of the battery. In all modes of transportation, LIBs are classified as dangerous goods. This is increasingly problematic as at the moment most LIBs are produced in South East Asia meaning that the majority has to be transported long distances as usage is spread all across the world. Currently the industry-standard is to limit the SoC to 30% to minimise potential risks. [52]

Lastly, the chemical compounds in the battery pose a risk. If there is leakage some compounds will react with the environment. For example, the liquid organic electrolyte if exposed to air will react with the moisture, and form hydrogen fluoride which is corrosive and very dangerous for both the cell and human alike. The chance of this happening at room temperature is small, but increases significantly with elevated temperatures. The organic electrolyte can also burn in the air as it is flammable. [14]

Applications and Projects

As the current market standard, the LIB is utilised in many projects. To name a few, one of note is the Hornsdale Power Reserve, which is the world's first big battery according to themselves [53]. This 100MW/129MWh BESS provided by Tesla has the purpose to facilitate the integration of renewable energy in the Southern Australia state, and supposedly auxiliary services [54]. It has since its construction been expanded in 2020 with another 50MW/64.5MWh also provided by Tesla.

Another project of note is the Kearny Energy Storage Facility in California, with a size of 20MW/80MWh that utilises a LFP system, which aim to be charged with electricity from the grid during excess and then discharged when needed, usually during night [55].

2.3.2 Vanadium Redox flow Batteries

Overview of the Technology

The All-Vanadium Redox Flow Battery (VRFB) is one of the most mature technologies in the flow battery category. A VRFB works as a standard Redox Flow Battery (RFB), with the electrolyte split into an anolyte and catholyte in two separate tanks for the positive and negative side. As the name suggests, the VRFB use vanadium redox couples, V_2^+/V_3^+ on the negative side and V_4^+/V_5^+ on the positive half-cell, to store energy. The electrolytic solutions are pumped around and into the core where the redox reaction occurs, and H^+ -ions are shared. [24]

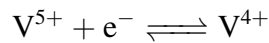
The special ability of vanadium to be soluble in four different oxidation states is what allows the battery to operate only on vanadium [56]. The overall chemical reaction for the VRFB is the following [56]:



of which its half-cell reactions are:



Important to highlight is that in some literature, Eq.(2.6b) is sometimes shown as the following:



Materials

As mentioned, vanadium in four different oxidation states are used as the electroactive material, soluted into the electrolyte. The metal however is classified as a strategic material of which majority of its extraction is in non-european countries. Its limited availability has led to a very volatile supply and price. [56]

The electrolyte of which the vanadium is most commonly dissolved in is diluted sulphuric acid. How much of the vanadium-ions that can be solved strongly depends on the concentration of sulphuric acid as well as its temperature. It is often that additives are added to the electrolyte, such as phosphoric acid and ammonium compounds. These additives work as stabilising agents which allows for a more broad operating temperature range. [57]

The most widely used material for its electrodes is carbon-based materials. This is because of their good stability and low resistivity together with being low cost. It is however not perfect, as its electrochemical activity is poor. This is a problem for large-scale application. Therefore, much research has been done to improve its performance. [58]

Performance and Characteristics

VRFBs are known to have long life cycles with a high RTE of 90% at light load operation. Moreover, the key benefit is that it can maintain the same voltage

at all operating conditions and can be instantly recharged by simply replacing the electrolyte in the tanks. [24]

The use of a single metal in both electrolytes prevents cross-contamination and therefore allows for longer lifespans (15,000-20,000 cycles) than most of its contemporaries and solid-state batteries. It also have a short response time in the order of a millisecond. Although, its energy density is almost 10 times lower than LIBs, around 25-35 Wh/L. Specific power and power density is hard to quantify for a Redox Flow Battery (RFB), but the typical current density of commercial VRFBs are around $80\text{-}100\text{mA}/\text{cm}^2$, while its power density can just about reach $100\text{mW}/\text{cm}^2$. [56]

Sadly, VRFBs have low electrolyte solubility, even with additives. This hurts its performance and is why its energy density is rather low. Moreover, the electrodes that are used are porous, which may reduce polarisation and its energy efficiency. A less chemistry related issue is that it is hard to model VRFB systems, such as finding optimal electrical circuits and physical parameters. [59]

To conclude, an important question is its costs. The price of vanadium is currently a significant issue as the initial expenditures of VRFBs are far larger than say LIBs, where the material price is a significant contributor to it [59].

Sustainability, Environmental, Safety and Ethical concerns

As mentioned earlier, vanadium as a material is volatile in both price and supply. Even though vanadium is more abundant than, for example lithium, there are still questions regarding its availability. Around 90% of the material today is used by the steel industry, which is not expected to stop [60]. However, it has been forecasted that even if VRFBs would increase in deployment, there are enough resources available for the foreseeable future. However, the question is if production will be able keep up with an increased demand. An important feature related to this though is that vanadium is not consumed at all in a VRFB, which means that it can be recycled at will [56].

Applications and Projects

Vanitec, the largest global vanadium organisation list 26 companies of which provide VRFBs [61]. Recently, a 100MW/400MWh VRFB system was built and incorporated to the Dalian grid in China [62]. It is the first wave in the country's plan for large-scale VRFBs, as they aim to increase the aforementioned BESS to 200MW/800MWh at a later stage. Its role is to lowering peak load in the city and potentially on a provincial level.

Another large project is the Minami Hayakita substation in Japan, delivered by Hokkaido Electric Power and Sumitomo Electric Industries [63]. It is rated as 15MW/60MWh and used to enhance grid control with the addition of 162MW wind turbines. The application of **VRFBs** in the western world is not at the moment at equal scale, with various smaller applications in the range of 2MW with up to 20MWh capacity in countries such as Germany and the US [56].

2.3.3 Sodium Sulphur Batteries

Overview of the Technology

One of the more mature battery technologies on the market today is the **Sodium Sulphur Battery (NaSB)**. It was first developed in the 1960s by Ford Motor Company. Molten- sulphur and sodium are used for the positive and negative electrodes respectively. The electrolyte is solid beta alumina ceramic as well as the separator between the two electrodes. The sodium ions from the positive electrode are the only thing allowed through the electrolyte and goes through recombination with sulphur when it reaches the negative side, which forms sodium polysulfides. When sodium ions are created at the positive electrode electrons are formed as well, which produces a voltage of 2.0 V. [24]

The full reaction taking place at the electrodes is the following [64]:



of which its half-cell reactions are:



Materials

The **NaSB** is different from most familiar battery systems, as it uses liquid electrodes which are separated by a solid electrolyte, a so-called L/S/L configuration instead of the more common S/L/S (Solid/Liquid/Solid) configuration [65].

The solid membrane separator in a **NaSB** is made from β -alumina, which are oxides that are characterised by their structure, that have alternating and closely packed oxide slabs with loosely packed layers that contain mobile Na^+ [66]. Furthermore, two distinct crystal structures in the group are $\beta\text{-Al}_2\text{O}_3$

and β'' - Al_2O_3 , which are hexagonal and rhombohedral respectively. The latter one is preferred because of its superior Na^+ conductivity.

Performance and Characteristics

NaSBs possess high energy density in the range of 150-240 Wh/kg, as well as high power of 150-230 W/kg, and high coulombic efficiency. Moreover, it is a high temperature battery which operates in the range of 300-360°C and can perform up to 4500 cycles [67]. Furthermore, they have an **RTE** of between 70-85 [68]. They are also suitable for various applications such as load levelling, peak shaving, renewable integration, emergency power, and power reliability. A significant benefit of **NaSBs** is that the material used to fabricate them are abundant and relatively cheap. [24]

The heat loss from each battery module is approximately a self-discharge of 1% per hour, which does not make **NaSBs** ideal for long term storage. On the other hand, the response time of **NaSBs** is claimed to be <1 ms, if the battery is already at operation temperature, which suggests that there are energy losses in keeping it ready while idle. The temperature also needs to be kept stable to keep the electrodes molten. A potential benefit though is that **NaSBs** have significant pulse power capabilities, which means that they can operate at higher power than rated for short periods. However, it is only useful for some applications. [69]

There are some **NaSBs** that can be operated at room-temperature, which greatly lowers cost and saves energy. However, there are issues with short cycling stability caused by incomplete conversion of sodium polysulfides. One way to improve it is by using gold nanodots decorated on hierarchical N-doped carbon microspheres (CN/Au/S). This allows for long cycling stability and high-rate capacity. [70]

Sustainability, Environmental, Safety and Ethical Concerns

The highly active molten electrodes of sodium and sulphur are one of the larger safety concerns of a **NaSB** [71]. Sodium reacts extremely well with air and moisture, which usually leads to explosion and produces hydrogen gas (highly explosive) and sodium hydroxide (very poisonous) [72]. Moreover, even though sulphur is less reactive, it is easily flammable and can create other hazardous chemicals. The high operating temperature needed is also in itself a safety risk.

Applications and Projects

Mitsubishi Electric Corp built a pilot project in 2016, claiming a 50 MW output and 300 MWh rated capacity, which made it the largest **NaSB** in operation at that point. The goal was to balance the grid frequency disturbed by increased addition of renewable energy sources to the local grid in Buzen (Fukuoka prefecture). [73]

In 2019, Abu Dhabi started operation of that time's largest **BESS** – a 108 MW output and 648 MWh capacity **NaSB**. The battery will help the city's load balance during daytime and provide six hours backup for emergencies. [74]

Both installations have been built by NGK Insulators, which is the only manufacturer of **NaSBs** at commercial level at the moment. Figure 2.2 shows their most significant projects. As can be observed, even if they are only one company, many installations and projects have been started and are planned.

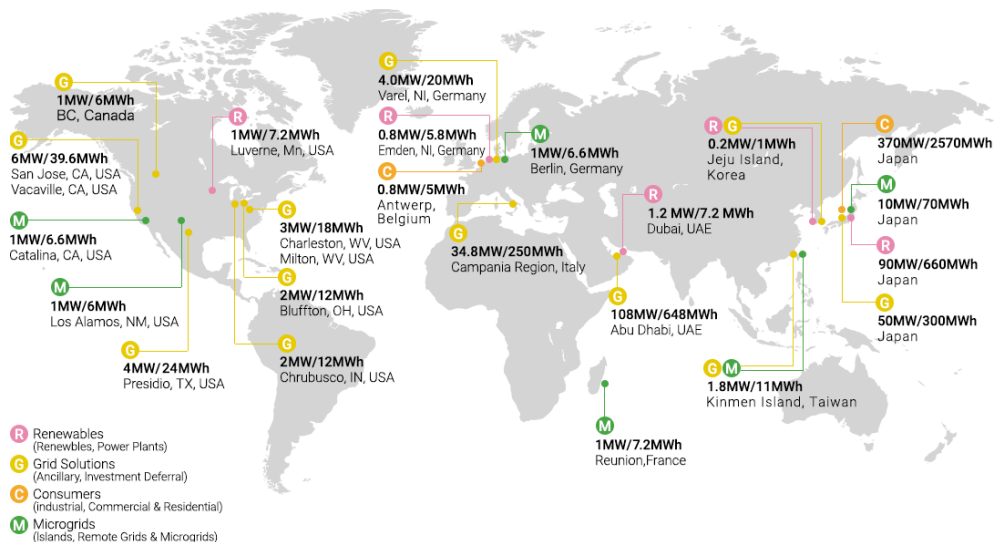


Figure 2.2: World map of Sodium sulphur battery systems installed by NGK Insulators as of March 2023, totalling 700 MW or 4.9GWh [75].

2.3.4 Sodium-ion Batteries

Overview of the Technology

The easiest solution to the issues connected to lithium/cobalt in a **LIB**, is to use a more abundant material. This is the reason for why the **Sodium Ion Battery (NaIB)** has gained attention again, as a replacement. It was researched together

with the LIB in the 80's but was dropped because of lower performance. However, the advantage in material availability of sodium related to lithium is now more important, therefore the renewed interest. [76]

The working principle and reaction mechanics of this battery is almost the same as in a LIB, utilising insertion, and intercalation of sodium-ions to create voltage difference. However, since sodium-ions are larger than its lithium counterpart, there is more strain put on the volume and structure of its host [76]. The phase stability, transport properties and interphase formation are also affected [77].

Materials

Regarding cathodes, generally electrodes with a potential above 2 V vs Na⁺/Na are suited as cathodes for a NaIB. Historically, it was found that layered oxides of 3d transition metals were suited, such as NaCoO₂, Na_xCrO₂, NaMnO₂, and Na_xFeO₂. However, any further research stopped when the success of the LIB became apparent. Today, many of the methods and materials that have been developed for the LIB are available for the NaIB as well, meaning that there is a wide selection available when it comes to cathode material. These can be categorised into two major groups: layered metal oxides (which was mentioned above) or polyanion compounds. The latter one is characterised by properties such as good cycle ability, high electrode potentials and robust structural framework. [76]

When it comes to anode material, the most suitable one thermodynamically is metallic sodium. However, since there is an unstable formation of the solid electrolyte interphase on the electrodeposited sodium surface (and other issues), it has not been realised. Graphite which is used in the LIB is not available since it does not properly intercalate Na-ions [77]. Instead materials that can act as active material hosts, capable of insertion at potentials slightly above 0 V vs Na⁺/Na, are used. This includes carbon-based intercalation materials (such as expanded graphite or the state-of-the-art material hard carbon), titanium-based compounds (titanium dioxide or sodium titanates), alloy-based materials (with “p-block” elements) and lastly conversion-based (e.g. metal oxides and metal sulphides). [76]

The electrolyte that has been used in NaIBs so far is organic electrolytes, most commonly formulations such as NaClO₄ or NaPF₆ salts in carbonate ester solvents. However, because of the high reactivity with metallic sodium and heightened chance of dendrite formation, new types of electrolytes to use are sought for. One such case is aqueous electrolytes, which were

used recently and demonstrated good performance. However, the type is more complex than its organic counterpart when used in similar systems. In any case, the required properties for an electrolyte are the following: stable (chemically-, electrochemically- and thermally), ionically conductive, electronically insulating, and low toxicity. Preferably low production costs as well. Other electrolytes that have been investigated is polymer- and all-solid electrolytes, both with varying success. [77]

A final thing to point out that has a large influence, is that aluminium can be used instead of copper in a NaIB as current collector material. This means both a reduction in cost as well as weight and allows for better storage and transport capabilities than LIBs. [78]

Performance and Characteristics

A NaIB has capabilities for various discharge rates, even when designed for energy applications in contrast to power [78]. Depending on material- and design choice, the average specific energy of a NaIB is around 100 to 200 Wh/kg, with working voltages as high as around 3.5V [79]. Non-aqueous NaIBs have been shown to achieve 2000-3000 cycles while aqueous variations have some reaching as high as 35,000 cycles.

Moreover, a specific commercial NaIB have shown an energy density of 290 Wh/L for a 32 Ah pouch cell, as well as a specific power and power density of 1000 W/kg and 1300 W/L respectively. The battery has a RTE above 93%, which is similar to a LIB. Furthermore, because of more abundant materials, the so called "bill of materials" of a NaIB is between 25-30% lower than a LFP specifically. [79]

Sustainability, Environment, Safety and Ethical concerns

The whole point of the resurgence of interest in NaIBs is because of the larger abundance of sodium than lithium, both in availability and ease of extraction.

Something that is key for a sustainable and environmentally friendly battery is recycling. However, in contrast to the large data on recycling of LIBs, data for NaIBs is scarce. The recycling of a NaIB is even more important, as fresh production of a NaIB have more associated greenhouse gas emissions than for a LIB on average. A large reason for this is because the LIB have higher energy density. Overall, it currently looks like that the NaIB will not be able to compete with the LIB when it comes to GWP, although the distance between the two should decrease as the technology develops and matures. [80]

When it comes to safety, in contrast to its LIB counterpart, NaIBs can be at any SoC during transport [81], because of the aluminium current collectors. Self-heating behaviour of a NaIB has also been shown to occur around 260°C which is 100°C higher than LIBs, which showcase their superior thermal stability [82].

Applications and Projects

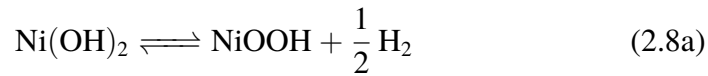
There are many companies around the world that are trying to commercialise NaIBs, some interesting ones are mentioned here. First one to note is Faradion Limited, that is a subsidiary of India's Reliance Industries [83]. Except stationary storage solutions, they also provide battery solutions for transport and smaller scale. Another company of interest is HiNA Battery Technology Company (offshoot of the Chinese Academy of Sciences), which have built a 100 kWh NaIB storage plant and put it into operation in Jiangsu Province, China [84]. The plant is used for peak shaving. Lastly, the Chinese automotive battery manufacturer CATL have announced that they will provide a NaIB for the market in 2023, promising 160 Wh/kg of energy density and other attractive characteristics [85]. However, their aim is on batteries for mobility and the potential of their batteries for large-scale is not clear.

2.3.5 Nickel-Hydrogen Batteries

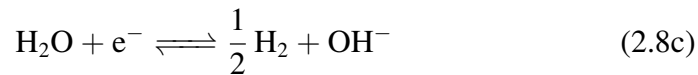
Overview of the Technology

Nickel-based batteries has been in discussion ever since the invention of the Nickel-Cadmium battery 100 years ago, and long history of use in satellites. Despite their age, nickel-based batteries still offer some advantages in performance, such as high stability, longer operating life, and being capable of handling extreme temperatures. A Nickel-Hydrogen Battery (NiHB) can be distinguished from nickel-metal hydride batteries by its use of hydrogen in gaseous form. However, similar to its siblings, Ni(OH)_2 is still used as the positive electrode, while the negative electrode in contrast is gaseous hydrogen. The electrolyte in use is strong alkaline electrolytes [86], such as potassium hydroxide (KOH). NiHB has been considered as a hybrid technology because of its anodes current similarities to fuel cell electrodes. The difference is that the gaseous hydrogen is stored in the battery at all times. Because of this, a durable case is needed to be able to with-stand high pressure. [24]

The full cell reaction taking place at the electrodes is the following [86]:



of which its half-cell reactions are:



Materials

The most abundant element in the universe is hydrogen, which means that there are no threats of material scarcity when it comes to the negative electrode. The **Hydrogen Evolution Reaction (HER)** and **Hydrogen Oxidation Reaction (HOR)** which takes place at the negative electrode are two of the more largely explored reactions because of their prevalence. However, for the reactions to take place catalysts are needed. The best **HER/HOR** catalysts currently are metals from the platinum-group. Although, because of their scarcity and cost, other options are currently investigated. For example, a large amount of low-cost catalyst in alkaline solution has been reported recently, which could prove useful in **NiHBs**. Another choice that is widely studied is transition metal compounds, such as Ni-based alloys. [86]

In a similar vein, the Ni(OH)_2 positive electrode and the conversion of $\text{Ni(OH)}_2/\text{NiOOH}$ has a long history of research and development from years used in space, which is the reason for its industrial maturity and durability [86]. Ni(OH)_2 itself exists naturally, as its mineral form was first found and identified in Greece 1981 [87]. Nickel as a metallic element is the fifth most common element on earth and is abundant in the earth's crust and core [88]. Moreover, it is also easily recycled, and around 80% of it in history has been mined the last three decades. One point though is that as of late nickel has been viewed as a critical mineral, such as the US which has included it in their list of critical minerals [89]. Similar to lithium, this is driven by the expansion of electric vehicles, of which it is expected that the nickel demand will increase by 14 times until 2030 [90]. However, just as demand has increased, the supply have steadily increased as well [91].

A final thing that is important to highlight for the **NiHB** is that cobalt is sometimes used for the cathode material as an alloy with nickel [92], as it can boost performance. Although, some try to stay away from it, such as

Enervenue/Schlumberger, which in an interview stated that they stay away from using cobalt, and if it is used it is only as part of a nano-thin alloy layer [93].

Performance and Characteristics

A significant benefit of **NiHBs** are their very long life-time, which has allowed them to be used in space [86]. They are said to be durable for 20,000-30,000 cycles [24, 93], and have achieved up to 40,000 cycles in low earth orbit satellites [86]. Historically, when used for aerospace applications, the **NiHB** has showcased almost no degradation to its capacity even over 30,000 cycles [92]. Moreover, it has a specific energy of 40-75 Wh/kg [24, 86, 94], and an energy density of 60 Wh/L. They also possess high charge/discharge efficiency of 85% [24], on top of good capability for being over-charged/discharged without safety issues [94]. Because noble-metals are usually used to increase the **HER/HOR** reactions, in addition to other costly materials and its design, the battery has been relatively expensive which is why it has primarily been used in space projects. However, some claim that they can achieve costs as low as USD83 per kilowatt-hour [92], although based on lab-scale.

A special characteristic to consider for **NiHBs** is the use of hydrogen gas. It has to be contained in a pressurised vessel and at least for space, the maximum which have been used is slightly over 80 bar [24][95]. The pressure of the hydrogen itself has a large influence on the rest of the battery, such as being directly proportional to its self-discharge rate. However, for typical space operating temperatures of 0 to -5°, the rate is low, even for pressures of around 70 bar [95].

Sustainability, Environmental, Safety and Ethical Concerns

Even though hydrogen is a popular element to use for green technology, it is still a very flammable gas which can cause fires and even explosion when not handled properly [96]. It is also hard to identify, as it is a colour- and odourless gas. Furthermore, because of its light weight there are no odorants that could be added that would diffuse at the same rate as hydrogen to make it identifiable. Another thing is the utilisation of cobalt by some manufacturers, which has already been discussed for the **LIB**.

Moreover, unlike most other batteries, the use of a gas as electrode causes design hurdles and strict pressure containment. Keeping 70+ bar consistent is difficult, however, its long history in use and proven durability, shows it is possible to operate it safely. Regarding Ni(OH)_2 , it might cause lung damage if exposed to it in a single instance, or by repeated lower exposures [97]. Lastly,

Table 2.15: Environmental impact of Nickel from production [98].

	Per kg Ni
Global Warming Potential	13 kg CO_2 -eq
Primary Energy Demand	236 MJ
Blue Water Consumption	106 kg

because it’s a low temperature battery there are no large risks in fire hazards, and overheating is not likely.

When it comes to its sustainability and environmental impact, it is hard to say as there are no studies in literature who has investigated the **NiHB** specifically. However, Nickel Institute has done a life cycle analysis on the impacts of nickel as a material [98], which findings are shown in Table 2.15.

Applications and Projects

Enervenue is the only company who currently offers **NiHBs** commercially. The start-up company begun in the summer of 2020, which is now set to deliver 50 MWh of capacity in 2023, and additional 100 MWh each year for two years after [99]. Last year in June, the company also agreed to provide **NiHB** systems to Puerto Rico’s Sonnell Energy Solutions, 40 MWh in 2023 followed by 420 MWh in 2024 and 2025 [100]. Since 2021, Enervenue is in collaboration with Schlumberger for development and deployment of their product [101].

2.3.6 Zinc-Bromine Batteries

Overview of the Technology

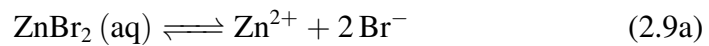
Zinc Bromine Flow Battery (ZBFB) belong to the category hybrid flow batteries, which is considered to be a combination of secondary batteries and flow batteries. Cells of this category contains one battery electrode and then one fuel cell electrode. The two electroactive materials behave in different ways, one electroactive material is inside the electrochemical cell and plated as a solid, which resembles the common metal battery electrode. The other electroactive material share likeness to fuel cell electrodes, as it is dissolved in the liquid electrolyte. The electrolyte is pumped to the cell from an external source and then back in a cycle. [24]

Specifically, for **ZBFBs**, the electrolyte is a zinc-bromine solution stored in both tanks on either electrode side. Bromine is always dissolved in the electrolyte on the positive electrode side. On the negative side though, zinc

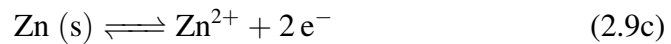
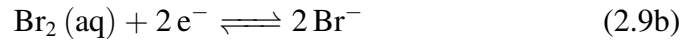
is only solid whenever the battery is charged, but during discharge the zinc is dissolved into zinc-ions. The solid zinc is deposited onto the negative electrode. [56]

In between the two electrodes is the separator, which is a conductive plastic. The component is important, as it defines the amount of diffusion of bromine to the negative side and therefore the coulombic efficiency. [102]

The full cell reactions that take place at the electrodes are shown below, its cell voltage is 1.85V [56]:



of which its half-cell reactions are



Materials

The electrolyte in ZBFBs is as mentioned zinc-bromide. The material is dissolved in water to form the aqueous solution and then used in both cycles for cathode and anode during operation. Zinc-bromide in the solution is usually of high concentration, around 1-3M but possibility to go as high as 4M. The variation in concentration is inherent from the fact that Zn^{2+} is reduced (deposited) during charging, while the Br^- is oxidised and therefore the zinc-bromide concentration decrease. Since bromine is toxic and corrosive, a complex agent is added to the electrolyte to sequester bromine into an alternate phase with low vapor pressure. This prevents bromine from escaping the electrolyte as a vapor and interacting with the rest of the cell as its elemental form. [103]

Both zinc and bromine are low-cost materials and there already exists industrial production for the two [103], meaning that availability pose no threat. However, the sequestering/complexing agents needed for the toxic bromine are expensive which increase the overall cost [56].

Performance and Characteristics

ZBFBs posses attractive characteristics for large-scale deployment. Since it is a RFB its power and energy is decoupled, meaning it can be scalable as desired. Furthermore, it possesses a specific energy of 60-85 Wh/kg [104]. This is on the lower side however with room to improve as it is only 20% of the theoretical

limit. However, the power density is fairly low, primarily because of the low conductivity of the electrolyte producing large internal resistances and high polarisation in the positive electrode [105]. Moving on, its DoD capability is good and can handle a discharge duration of 8-10 hours [24]. What could be better is its relatively low RTE range of between 60% to 85%, although it is expected that it will be better in the future [11]. Because of utilisation of low-cost materials, the ZBFB shows great promise as an inexpensive alternative for energy purposes. Although, its cost of power is significantly higher than the other batteries mentioned, where some sources claim USD890/kW or up to USD2,000/kW [43, 106].

Theoretically, its cycle-life has no limit since the electrolytes do not suffer ageing effects. It is claimed that it is capable of up to 10,000 cycles [11], while another source states it is capable of 3650 cycles [43]. However, a large caveat to its life time is that it has to be fully discharged every few days otherwise dendrites will form, and it also needs to be short-circuited and to periodically be shorted at its terminals while pumping the electrolyte to fully remove zinc from the battery plates [56]. This shunting is required between 1-4 cycles after a full discharge, and the process can take between 0.5-2 hours (affected by temperature and use history) [107]

Sustainability, Environmental and Safety and Ethical concerns

To begin, its environmental impact was assessed in the study by He *et al.*, in 2020 [108], the GWP of a ZBFB was 0.158 kgCO₂-eq/Wh while its CED was 1.99 MJ/Wh, which are both relatively low. Together with its benefit of the largely abundant materials that are used, the ZBFB is somewhat a sustainable alternative when it comes to batteries. A pain-point however is the titanium-based bipolar plate that is used [108].

As previously mentioned, bromine is toxic and corrosive which pose some safety risks. This is reduced by the addition of agents, however, the complex agent only appears to be stable if temperatures stay below 50°C (5°C safety margin). Except for in the case of fire, it is unlikely that temperatures could reach higher than 50-60°C, and even the chance of a fire is unlikely, as the electrolyte is non-flammable. Because of the belief that the system is very safe, many manufacturers do not include a Heating, Ventilation and Air Conditioning (HVAC) system, which is used to combat fire. This is potentially concerning, especially for applications in hotter climates with an elevated ambient temperature. [109]

Applications and Projects

Redflow is the largest provider of **ZBFBs**, with a total installed capacity of 2,959 MWh over 285 active projects [110]. Its largest project is a 2 MWh **BESS** comprising of 192 **ZBFBs** for Anaergia, Inc. Its purpose is to reduce peak energy use at Anaergia's Rialto Bioenergy Facility in California [111]. Another manufacturer of **ZBFBs** is Primus Power, who recently launched their second generation **ZBFB** apply named "EnergyPod 2" [112].

2.3.7 Metal-Air Batteries

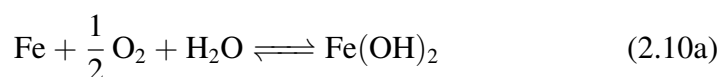
Overview of Technology

Metal-air batteries is the name for the various batteries that utilises ambient air as a cathode in conjunction with a metal electrode such as lithium, zinc, aluminium etc. Their main benefit being that they are some of the most inexpensive and compact batteries today [24]. Two variations of this technology are presented down below.

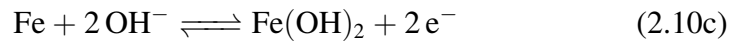
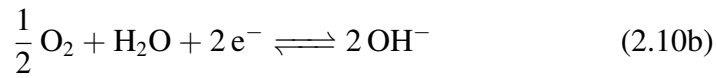
Fe-Air Rust Battery

A fundamental chemical process that has long been the nuisance for metalworkers is rust, the oxidation of iron. However, this process can be utilised for energy storage as proven by the **Iron-Air Battery (FeOB)**. The battery is similar to redox flow batteries at least with its positive electrode, which is ambient air flowing through the electrode as the electrolyte in a redox flow battery. The main benefit of this is that no external tank is needed for the reactant, which reduces the design complexity. The iron electrode on the other hand resembles the conventional standard electrode design with an active material. In the 70s and 80s various organisations and companies pursued this technology to be used in electronic vehicles. However, the limitations at that point were too significant for that use-case and development were dropped. Although, the advantages of this technology in large-scale **BESS** are compelling – such as its low cost and safety, which is why there is a resurgence of attention given to it. [113]

The overall cell reaction taking place at the electrodes is the following, with a voltage of 1.28V [113]:



of which its half-cell reactions are:



Solid Oxide Metal-air Redox-flow Battery

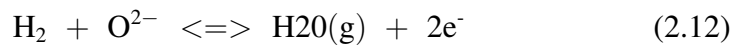
Another of the several metal-air batteries that is interesting is **Solid-Oxide Metal-Air Redox Battery (SOMARB)**, which was first demonstrated as a novel technology in 2011 [114]. This new chemistry was different from other solid oxide metal air batteries, as the new design featured a separated electrical charger and energy storage unit. This was introduced to avoid the significant issue of volume change that is associated with metal oxidation. It also gives flexibility in either designing the cell towards energy or power specific use-cases. [115]

The cell structure is made up by a **Solid-Oxide Fuel Cell (SOFC)** of tubular design, integrated with a redox-cycle unit. The inner wall of the tube is the anode material, while the cathode is on the outside of the tube as a mixed oxide-ion/electronic conductor. Inside the tube, a MeOx mixture together with some sort of solid porous metal (with high-surface area) is placed right next to the **SOFC**, operating as the functional redox material. Hydrogen and steam, products from the steam metal reaction, then flow through the **SOFC** as well as the redox-cycle unit, therefore creating a closed loop. The flow of reaction gas resembles the flow of the electrode liquid in a redox-flow battery and is why the battery is also called “redox”.

The overall discharge reaction (inside the metal-bed, which is key for the operation of the **SOMARB** is the following, as described by Xu *et al.*, in 2011 [114]:



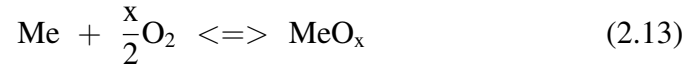
The hydrogen that is produced is then oxidised in the **SOFC**, which produces electricity and steam as shown in 2.12.



When the necessary amount of metal-phase has been oxidised, the battery is recharged. The high amounts of steam that was produced during discharge is now used to produce hydrogen at the cathode of the **SOFC**, meaning Eq.2.12 in reverse. The generated H_2 is then used again in the redox cycle unit to

reduce MeO_x to Me (meaning Eq. 2.11 in reverse) which can be used for the next discharge cycle.

By combining all reactions, the overall chemical reaction of the whole cell is then:

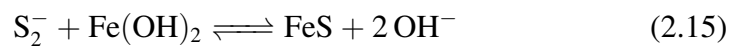
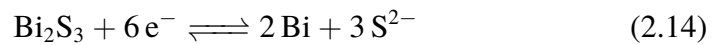


Material

Between the two versions described, both share the same characteristic of utilising iron and air as the electrode material. In the case of iron, it is the most abundant metal in the Earth [116]. Therefore, scarcity pose no threat and it is also a low-cost metal [117].

FeOB

To combat spontaneous corrosion of the iron in the negative iron-electrode, Bi_2S_3 is used, which decomposes into its constituents during cycling (Eq. 2.14), of which the sulphide then reacts to form Iron(II)-Sulphide (Eq. 2.15). In total this reduces the HER and the formation of Iron(II)-Sulphide increases conductivity. [118]



The common electrolyte to use is alkaline electrolytes such as KOH, since it has good electrical conductivity and is not too corrosive to the iron electrode. Because of low solubility of oxidation products from the iron in the electrolyte (such as $\text{Fe}(\text{OH})_2$), dendrite formation is avoided [117]. Moreover, like all metal-air batteries, an FeOB requires a membrane that acts as a barrier to stop CO_2 and H_2O from entering the cell as to avoid corrosion and carbon poisoning [119]. The positive “air” electrode is required to achieve both Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR), since otherwise two electrode materials would be needed for charge and discharge respectively. Therefore, a bi-functional electrode is necessary [117]. Furthermore, because of the slow reaction rate of ORR, a strong catalyst is needed. This unfortunately means that the list of non-noble catalysts available is limited, and even more so when demanding high-performance OER of the catalyst [118].

SOMARB

The materials that are used are the same as for conventional **SOFCs**, *e.g.*, lanthanum-strontium-cobalt-ferrite base oxygen electrodes, nickel-based fuel-electrodes and zirconium-dioxide based electrolytes [115]. Otherwise, there have not been much research surrounding potential materials.

Performance and Characteristics

FeOB

Metal-air batteries are interesting because of their high theoretical energy density in combination with the benefit of that they use oxygen from the ambient air, which reduces their size and volume. A **FeOB** for instance has a nominal voltage of 1.28V and a theoretic volumetric energy density of 9700 kWh/L, much higher than say a **LIB** [120]. Although, its theoretical gravimetric specific energy is 1080 Wh/kg [121], which is lower than a **LIB**. Nevertheless, The technology also display great capabilities for deep discharge and only minor tendency for dendrite formation during repeated charge/discharging [122]. In practically though, the **FeOB** have a moderate energy density of 50-75 Wh/kg, and low efficiency at 50% [113]. It's cycle life at the moment is between 2,000-3,500 [113, 118], which is not very much. It has been shown though, that adding sulphide additives to the iron electrode could improve cyclability [123], and it is also known that the iron electrode is very robust and capable of 10,000 cycles [124], meaning there is room for improvement. Furthermore, the low efficiency is partly due to the unwanted **HER** reactions at the iron electrode as well as high over-voltage (0.5V) at the air electrode [124]. It also has a significant self-discharge of 20% loss in capacity over 14 days [113]. The current specific power of a **FeOB** is not available in literature, as the only recorded information that is available is from 1997 which says the iron-air cells, developed by Matsushita Battery Industrial Co. and by the Swedish National Department Co., displayed an energy density of 80 Wh/kg at C/5 and a specific power of 30-40 W/kg [125]. It should be expected that this has been improved since then.

SOMARB

The performance and special characteristics of the **SOMARB** is still in early research. Xu *et al.*, first reported on the proof of concept of **SOMARB**. It was stated that with a tubular design, for a operation temperature of 800°, it showed a specific energy of 348 Wh/kg-Fe(38.5%) and a **RTE** of 91.5% for

20 cycles [114]. Another article by Zhao *et al.*, made an attempt at a lower operation temperature, 650°, which during 100 cycles produced an average specific energy of 760 Wh/kg-Fe with a much lower RTE of 55.5% [126].

Sustainability, Environmental, Safety and Ethical concerns

In the case of the FeOB, it has many good aspects. This includes abundant and inexpensive material, requires less storage since it utilises ambient air and the mining of most resources pose no risks or have significant ethical problems related to them. Regarding SOMARBs, there are slight safety issues in the high operation temperature, but not something out of the ordinary. The GWP and CED from production of neither type is available in the literature. However, the parameters are available for pure iron and can be observed in Table 2.16.

Table 2.16: Environmental impact of Iron from production [127].

	Per kg of Fe
Global Warming Potential	1.5 kg CO2-eq
Cumulative Energy Demand	24.73 MJ

Applications and Projects

First of all, there are no current projects of significant size of SOMARBs that could be found, as it is still a largely unexplored technology except in academia. In contrast, for the FeOB the most notable company currently that offers commercial FeOBs is Form Energy, which was started in 2017. So far there is a lot of mystery surrounding the company and their product, as they have not disclosed a lot of information to the public. An interview was held with an employee at the company [128], who stated that they are supervising their first externally fielded system (outside of a Form Energy facility) this year, the Greater River Energy project. It is expected to come by 2024. The battery will not be cycled for economic potential, as it is more of a technical demonstration. Not mentioned in the interview, but the battery system will be 1MW and capable of 150 hours of discharge according to other sources [129]. Same source states that they have acquired another contract with Georgia Power Co, to which Form energy will provide their battery. They are also working with another company called ArcelorMittal for their iron materials. However, it is undisclosed when or where their first factory is going to be built [130].

Chapter 3

Methodology

As can be observed in the background, there are many batteries that have already proven themselves to be suitable for grid-scale application or is about to. Since there is not enough time to rigorously discuss them all in detail, certain criterion are set and will be used as tools to decide on which three alternatives that are believed to be of most interest to further analyse.

To begin, the aim of this report is to investigate up and coming battery chemistries that will be available and suitable for grid-scale deployment in the coming 5-10 years. Therefore, only batteries that are still not fully mature will be looked at. The chosen way to distinguish this will be by the **TRL**. It is believed that for a chemistry to be ready or to be of use in the coming 5-10 years, it must have reached at least level 6 or 7 by the end of 2023, as that means the technology is proven specifically for its use-case and does not require any new pilot projects taking place.

Furthermore, another criterion to consider is the cost of the technology. As proven many times in history, performance is not everything. In most cases, excluding high-capital projects such as spaceflight, the cost of a technology has at least around the same influence as the performance. Therefore, a selected battery should have a potential of low-cost (i.e few noble metals or other expensive material).

Another comparison tool is that the battery should be suited for long-term storage and long-term life. In short this means that the battery should have good energy density and capability for performing many cycles. Other good performance characteristics that are looked for includes low self-discharge and **RTE**. Moreover, technologies that are deemed to similar to **LIBs** will be omitted from deeper analysis. This is because there is already a large focus on ion-batteries in other works, and that this work aims to widen the overall

discussion, which means looking at completely new alternatives.

Lastly, for some of the studied batteries there is no literature on their actual **GWP** and **CED**, which are the two values primarily used to assess environmental impact and sustainability. In those cases, it is instead calculated by basing the values for the battery on the main metal that is used in the battery. The calculations for these are found in the appendix.

Chapter 4

Analysis

This chapter will first evaluate which of the detailed batteries in Section 2.3 that are of most interest as alternatives to LIBs. This is then followed by an discussion of their suitability for the various applications and services of which are described in Section 2.2. Lastly, there will be a specific case provided by Vattenfall, for which the selected batteries will be analysed and contrasted to a specific LIB chemistry.

4.1 Evaluation of Described Batteries

The aim of this section is to evaluate the potential of the mentioned alternative batteries in Section 2.3 to the LIB. Whether they have qualities for stationary or large-scale application, constrains or unique aspects and if they are mature enough or too mature.

4.1.1 Vanadium Redox Flow Battery

At this stage it is clear that VRFBs are an up and coming alternative for large-scale BESS. The size of applications, either as pilots or commercial projects, proves the large interest in the technology. Although, this means that it can be argued that it has a TRL of at least level 8, which is a bit above what is intended to be analysed in this report. Therefore, even though VRFBs show great promise for large-scale BESS, it will not be selected for deeper analysis. Also, the overall consensus is that it already is an alternative, therefore, it is believed that analysis and exploration of other alternatives could bring more fruitful results.

4.1.2 Sodium Sulphur Battery

There are currently not as many companies working on **NaSBs** as on **VRFBs**. However, it is still very much in discussion and NGK Insulator is instrumental for it. Regarding its maturity, the plethora of already installed projects and plants should put the **NaSB** at around **TRL** level 8 – which again is slightly too high for it to be qualified for further analysis. On top of that, there are still clear shortcomings of the technology, such as significant heat and energy losses per hour. This is minimised by room temperature alternatives, but they come with their own limitations, as described previously. Overall though, the capability of **NaSB** is good and could be further explored in another work.

4.1.3 Sodium-Ion Battery

Largely already proven by the success of its lithium counterpart, **NaIBs** shows great potential in the coming future. However, it will not be selected for future analysis largely because of its similarities to the **LIB**. This is because as stated, the aim is to find new alternatives and it is believed that it is of more interest to investigate batteries that does not function the same as other ion-batteries. Otherwise, it is an interesting alternative.

4.1.4 Nickel-Hydrogen Battery

The long historic use of **NiHBs** in satellites proves their capability. One could argue that the technology is already mature and that it is at level 9 for **TRL**. However, their usage has been specific in satellites and not for large-scale. Therefore, it is believed that the technology should be considered an "up-and-coming" battery chemistry for the applications that scale. Moving on, other benefits is that the materials which are used in **NiHBs** are readily available. Although, the reason for why they have been almost exclusively used in space is because of cost. However, the recent cost reductions of its materials, such as catalyst and other components, has made it more competitive. Because of this, it could be argued that it should no longer be considered high-cost. This is proven by the increase of companies trying to commercialise the technology. Regardless of cost or other factors, their performance and characteristics are all very much suitable for large-scale. For instance, the cycle life is basically unmatched. Because of this, **NiHBs** are believed to have a possibility to be an alternative to the **LIB** in the near future, and will therefore be further analysed.

4.1.5 Zinc-Bromine Flow Battery

A **ZBFB** is in many aspects a suitable candidate for large-scale **BESS**. It is a technology with a long history, but only a small list of producers and not many large-scale projects to note. Another review puts the **ZBFB** at **TRL 6**, which is viewed as an appropriate conclusion of its maturity [44]. However, there are some questions regarding their use. Even though their performance parameters are suitable for large-scale storage, such as theoretically endless cycle life and high theoretic energy density with low costs, the significant limitation of a full discharge every few days limits the ability to store energy for a long duration. Although, this is not as significant in some use-cases, or could be circumvented by design choices. Therefore, it is believed that **ZBFBs** makes an interesting candidate for further analysis as an alternative to the **LIB**.

4.1.6 Solid-Oxide Metal Air Battery

As previously mentioned, there are no current demonstrations and from what can be found no planned ones either for the **SOMARB**. Therefore, the technology is not in a state where it can be used commercially for large-scale **BESS** in the close future and will therefore not be selected for further analysis.

4.1.7 Iron-Air Battery

The notion of utilising rust for energy storage is fascinating. However, the **FeOB** is currently not at a stage where its performance is really competitive, with only moderate performance compared with current commercial **BESS**. Although, if its environmental friendliness, abundant materials, low cost, ease of scalability and safety is considered, its outlook is not as grim. These qualities are also what is sought after for an alternative to **LIB**. Moving on, since there are currently no significant projects of note for this technology, the question is then if it will be available in the coming 5-10 years. Form Energy as mentioned is set to build their first external installation of **FeOB**, which if successful could increase demand and availability of this technology in the close future. If strictly looking at its **TRL**, the **FeOB** is believed to be at level 5 at the moment. However, this could change quickly and there is still a possibility that it could reach **TRL 8** or **9** in the coming 10 years. Therefore, including all its advantages that have been mentioned so far, **FeOB** will be selected for further analysis as an alternative to **LIBs**.

4.2 Suitable Applications

In this section, the application of the **NiHB**, **ZBFB** and **FeOB** will be evaluated and analysed for the use-cases described in Section 2.2. First of, the **LIB** will be briefly analysed and then the alternatives are discussed on their suitability and how they compare.

4.2.1 Lithium-ion Battery

Out of all of the applications looked at, the **LIB** have already been used or show promise for it [11, 131, 24]. Its low self-discharge makes it good for applications with long storage duration (black start, backup power and local flex markets). Also, its chemistries possess a cycle life high enough for it to be a contender for applications where that is a requirement (load-control frequency services, energy arbitrage, peak shaving, renewable integration). An application of which it has not been used for is voltage control. Some sources claim though that it is promising for it [131], which is also believed by this author to be true, as it has been built in the same size range and it possesses the high power capabilities required. So overall, the **LIB** is a well performing battery with many suitable applications.

4.2.2 Nickel-Hydrogen Battery

Its excellent cycle life in combination with moderate to high energy density makes **NiHB** favourable for various applications. To start off, the battery is definitely suited for renewable capacity firming, as shown by its proven success in space, where it was charged by solar cells to power satellites while eclipsed. Specifically, the International Space Station circles the earth every 90 minutes, of which the satellite is in sunlight for 55 minutes [132]. This means around 50 cycles per day. There are few if any reasons for why this would not work in combination with solar parks on earth, which have only around 1-2 cycles per day. It is also believed that this is true for other forms of renewable power sources such as wind power, even though their load-profile is different. Overall, the **NiHB** seem to be on the same level as the **LIB** for this application.

When it comes to using a **NiHB** for regular and renewable energy arbitrage, the daily cycle of charging and discharging at similar times share a likeness to the cycle schedule in satellites, although less frequent and longer charge/discharge duration. Furthermore, from Ara Ake's report on battery

systems for energy arbitrage [43], it is claimed that based on market data from 2022, the capital cost of energy for a **NiHB** is USD330 per kilowatt-hour , which is in the same range as a **LIB** [43]. This means that potentially a **NiHB** could be less costly than a **LIB** because of its longer lifetime. It's efficiency is also not that much lower. Therefore, one could claim that for energy arbitrage, the **NiHB** is the better option.

In the case of using a **NiHB** for load-frequency control services, its cycle stability makes it promising for most variations, except for **FFR** as the discharge rate is too harsh. Otherwise, it can discharge for at least an hour and start quick enough for it to fulfil all of the other regulation services as detailed in Table 2.3. This puts it on the same level as the **LIB** except for **FFR**.

Regarding peak shaving, the requirement of 300-400 cycles per year is not an issue for **NiHBs**, and it is also capable of up to 6 hours of discharge. Moreover, the storage duration is rather low. Therefore, its high self-discharge is not as much of an issue, although still significant to be noticeable. However, it is believed to not be so bad as to not say that it is not suited for it or that it is not equal to the **LIB** for this application.

Applications where high self-discharge becomes more decisive includes black start and backup power, which means that it is unsuited. Otherwise, there are no shortcomings that could hinder it to be used for either application.

Local flex markets should also be included as unsuitable since only a few cycles for a 5 month period is what could be expected as of now. However, if more cycles are performed or if the self-discharge of a **NiHB** decrease it could make it suitable.

Another case where it is unsuitable is voltage control, which in this case is because of its low discharge rate capability. Furthermore, the frequency of cycling is only around 1 per month, meaning that the storage duration is again too long.

For congestion management, the self-discharge of a **NiHB** do have an influence. However, if it is operated around 100 cycles then the influence is not as noticeable, and its very long lifetime could be a trade-off. Moreover, since the technology is very safe, and rather oblivious to its surrounding environment, it then makes it not very geographically reliant which is a benefit compared to the **LIB** which is less safe. Furthermore, the required discharge duration and size capacity are definitely possible by a **NiHB**. Therefore, it is concluded that the **NiHB** is at least equally suitable as a **LIB**, and have great potential to be more suitable if its long-term storage capabilities are improved.

4.2.3 Zinc-Bromine Battery

To start of, a significant constraint for the **ZBFB** in many cases described below, is that the battery has to be fully discharged at least once a week, as previously described in Section 2.3. Applications that require storage longer than a week are concluded to be not suitable for a **ZBFB**. This includes black start, backup power, some frequency regulation applications (as will be explained a bit more below), local flex markets and voltage control. Long-duration storage is also not realistic, as its self-discharge is currently too high. This constraint is also a hindrance for applications of which high activity and shallow discharges are common with no opportunity to fully discharge.

For frequency regulation, because of the inherent inertia to start pumping the electrolyte, rapid response applications are not very feasible, such as **FFR** [11]. However, if the electrolyte is already in circulation, then **ZBFBs** are quick to respond in around a milli-second, in line with the **LIB**. For applications with long unknown periods in between sessions means it is not feasible though, such as **aFFR**. This only leaves **FCR** activities, of which all their technical requirements should be met, with addition of a full discharge each week to satiate the weekly demand. Overall though, the conclusion is still that at the moment, the **ZBFB** is not very suited for frequency control in comparison to the **LIB**.

Regarding peak shaving, because of the decoupling of power and energy it is easy to scale the battery as preferred. An especially great benefit for this application, as the peak demand can change with time. Moving on, since it can be expected that at least one cycle per day will be performed, the constraint of a required full discharge once a week is not as much of an issue. Moreover, there is already proof that **ZBFBs** work for this application, since as mentioned in Section 2.3, Redflow have already built a functioning 2 MWh **ZBFB** for peak shaving. If compared to a **LIB**, they are fairly equal for this application. The slight difference is the weekly constraint, but that is believed to be counteracted by the longer life-time of the **ZBFB**. Though, if factoring in cost there is a case for using a **LIB** for higher power capacities since the **ZBFB** have much higher cost of power. Overall though, for technical requirements the conclusion is that they are equally suitable.

An application where the **ZBFB** has potential is for renewable integration. It is suited for renewable energy arbitrage, but especially suited for capacity firming of solar power, as the significant constraint of a weekly full discharge is not as much of an issue when there is room every day to fully discharge the battery. This is more of an issue for renewable energy arbitrage as you

want to discharge when it is lucrative. Moving on though, a **ZBFB** is definitely capable of a discharge duration between 1-3 hours as required in the two cases. Moreover, its cycle durability and long lifetime make it very capable of many cycles, either shallow or deep. Therefore, a **ZBFB** is definitely at least equally suitable as a **LIB**, with a slight benefit in potential lifetime but a drawback in cost.

It is also suited for regular energy arbitrage, for the same reasons as mentioned for renewable energy arbitrage. Moreover, since the system should be in operation at most times, the activation time is not an issue and it can respond quickly as required. Of course, once a week a full discharge has to be performed which should be timed to when there is profit. The low **RTE** of the **ZBFB** is a drawback however, especially when compared to the **LIB**. Again, in Ara Ake's report on battery systems for energy arbitrage [43], it is stated that the capital cost of power was USD 0-890 per kilowatt [43], which is a lot more than for a **LIB**. This means that it is probably only worth it at lower power ranges. The cost of energy at USD 335-456 per kilowatt-hour is much more reasonable though, and close to the same range as the **LIB**. Overall, the **ZBFB** is probably rather equal to **LIB** for this application for in lower power range.

In the case of congestion management, doing 50-100 cycles per year means that at least around 1 cycle per 7 days is performed and therefore the required full discharge can easily be performed either one of those times or forced after a week. What is a slight problem though is that self-discharge will have a significant influence on the capacity if the energy is stored over a long duration. Moving on, a discharge duration of 1-4 hours is not an issue. What could be a problem though is that building a **ZBFB** to meet the higher limit of the size range (100MW) would be very costly, but it is technically feasible though. Overall, the conclusion for this application is that the **ZBFB** is suited for it, but will probably only be worth it for the lower size range because of cost. In comparison to the **LIB**, it also have slight safety concerns because of the toxicity of bromide, which combined with a lower energy density limits its placement.

4.2.4 Iron-Air Battery

At the moment, there are some unknowns surrounding the performance of current state of art **FeOBs**. Most literature available is almost more than 8 years old. Although, as shown by the success of Form Energy so far (discussed in Section 2.3.7), it is not unrealistic to believe that progress has been made for

this technology over time. A significant parameter that is unknown though is the response time of a **FeOB**, which is important to know to be able to actually state whether it is suited for applications or not. During the interview with Form Energy [128], it was claimed that it possesses the same rapid response as most other batteries. Therefore, it will be assumed that it possesses the same response time as other metal-air batteries, which is in the milli-seconds.

Even though the self-discharge of a **FeOB** is better than either a **NiHB** or **ZBFB**, there is still too much loss in capacity if it is expected to store energy for longer than a week. Therefore, all applications with expected storage duration longer than that is unsuitable. This includes voltage control, local flex markets, black out and backup power. If not for this, the capability for upwards to 100 hours of discharge duration makes the **FeOB** very promising for at least black out and backup power, as most batteries, such as a **LIB**, can not reach as long of a duration.

For the various frequency control services, its low power capability makes the **FeOB** definitely unsuited for **FFR** and potentially both **FCR-U** and **FCR-D**, as they are also sub-hour in discharge duration. It could maybe see some use for **FCR-N** and **aFRR**. But the conclusion should still be that it is not very suited for it when compared to the **LIB**.

Moving on though, energy arbitrage with a **FeOB** has a lot of potential. However, at this moment 50% **RTE** is just too low to be reasonable. Where it is less of a problem though is for renewable integration, where a **FeOB** would shine at capacity firming, because of their ability for long duration discharge. After an interview with Form Energy, they have also stated that they are targeting this application, meaning they believe it is suited for it [128].

Another potentially good alternative for **FeOBs** is for congestion management. Slight problem is that the storage duration for this application is long enough for self-discharge to make a noticeable difference, at least when compared to a **LIB** which only see a minor loss in capacity over the same duration. Another thing is that it would only see use for the lower limit on the size range for this application, meaning around 1-10 MW. This is because of its poor power output.

Lastly, in the case of peak shaving, again a **FeOB** is very much suited for this application, as there are no technical drawbacks that would not make it usable. Of course a higher efficiency would make it a better choice as currently its not really competitive with other commercial batteries because of that. Moreover, a longer cycle life would be good since if it is only capable of 2,000-3,500 cycles, it will have to be replaced at minimum after 5 years, if it is supposed to perform 300-400 cycles each year. Although, the **LIB** does

not have that much higher cycle life, and the capital cost of a **FeOB** is expected to be much lower – meaning replacing the system is not as expensive.

4.3 Provided Case by Vattenfall

As mentioned in the section 1.1, Research Questions, a specific case provided by Vattenfall will be analysed to investigate how the chosen alternatives compare to current **LIB** technology. It will start with an overview and background information followed by the technical requirements and economic characteristics of the battery systems.

4.3.1 Background and Technical Requirements

The case as provided is a theoretical offshore wind park case, in which a smaller wind park will be installed together with a larger wind park system. A battery will be installed as well, to assist the smaller wind-power system by storing excess energy and deliver it when needed. The power capability required is 20 MW, and it is meant to provide between 10-12.5 hours of energy, effectively meaning an maximum capacity of 250 MWh. It is also known that on average, it will perform 50 full cycles and 50 half cycles annually. The expected lifetime of the project can be said to be the same as a typical offshore wind park, meaning 30 years [133]. The planned start date by the company is 2030, which aligns well with the time frame of 5-10 years which is used in this work. Because of confidentiality though, more can not be stated at this moment about specific parts surrounding it. A quick summary of the requirements for this case are found in Table 4.1.

Table 4.1: Technical Requirements of battery for offshore wind park case

Power	20 MW
Energy	250 MWh
Discharge Duration	10-12.5hrs
Annual Cycles	50 full cycles 50 half cycles
Life time	30 years

4.3.2 Parameters and Assumptions

The equation and subequations for calculating the **LCOS** of a **BESS** have already been described in Section 2.1.3. Based on that knowledge, the following parameters are needed to effectively calculate the outcome for the systems that are analysed.

First parameter that has to be decided is discount rate, which is the rate at which money loses value over time. Most commonly, this is a fixed rate per year when working with projects that span many years. The discussion around what discount rate should be used, what affects it, and if it should change overtime is in itself a debate which is outside the scope of this work. Instead, to keep it simple it is decided that the discount rate will be 0.1 (10%).

Moving on, another value that is very much central to the calculation is the cost of electricity. Again, this value can change rapidly and it is uncommon for it to stay the same over long time periods. For this work, it is decided that the value will be based on the average price of electricity in Sweden during 2021, which is 57,89 €/MWh. This is for two reasons: In general, it is difficult to predict electricity prices even as short as a week into the future. Therefore, a constant price. Secondly, using an average value from 2021 is because the recent two years, the Swedish electricity market has been very unstable which, in combination with high inflation, has led to prices being very extreme and not a good indication of how it is "normally". As a consequence of this choice, it is also decided that the exchange rates that are used will be from 2021 as well. The fixed rates used are: 1 US dollar = 0.8458 Euros and 1 British Pound = 1.1632 Euros [134, 135].

Moving on to more technical questions, the degradation rate is typically something that is hard to generalise between cases. However, due to time constraints, the degradation rate of the two studied batteries will be based on another study by Storlytics [136], whom performed an evaluation study between **LFP** and **NiHB**. The technical specifications of that study are shown in Table 4.2. Their conclusion was that over the project lifetime, the **LFP** battery had a capacity reduction of 34.44%, in contrast to the **NiHB** who had an reduction of 6.80% to its capacity. This means an annual decrease of 1.722% and 0.34% respectively, and will be used as the degradation rate for this work.

Another thing that should be mentioned is that the battery degrade as it is utilised, meaning its maximum capacity will decrease over time. To compensate for this, the overbuild strategy will be assumed, which means that the built initial capacity should be high enough so that the battery's capacity never degrade below the required amount over its lifetime.

Table 4.2: Performance requirements for Storlytics case

Power	25 MW
Duration	4hrs
EoL Energy req.	100 MWh
Project Life	20
Cycle count per day	2.1
Cycle count per asset life	15,330

To calculate the actual rated capacity C_{rated} , Equation (4.1) is used, where $C_{required}$ is the required capacity and r_{dg} is the degradation rate.

$$C_{rated} = C_{required}(1 + r_{dg}) \quad (4.1)$$

The required capacity is by itself calculated by Equation (4.2), where P is the power demand and t_d the discharge duration.

$$C_{required} = P * t_d * DoD \quad (4.2)$$

Lastly, the technical and economic parameters that are used for the analysed batteries are collected in Table 4.3. As can be observed, the LIB chemistry that will be used for this case study is the LFP. The reasoning for this choice is because it has seen a rise in utilisation in the most recent years [137], and that it is believed to be suitable for large-scale because of its increased safety and longer cycle life compared to other LIB chemistries. The CAPEX is based on the capital costs as provided by Ara Ake (the value for LFP was taken as the average of the cost given for LIB) [43]. The calculation of the OPEX is calculated as £2/kWh of the required capacity [138], as that it is what is expected of a battery system above 100MWh capacity.

Table 4.3: Performance parameters used for the analysed batteries

Parameter	Unit	LFP	NiHB
DoD	%	80	97
RTE	%	92	85
Self Discharge	%/month	1	40
Annual Degradation	%/year	1.72	0.34
System lifetime	years	15	30
CAPEX	\$/kWh	311.5	330
OPEX	£/kWh	2	2

Chapter 5

Results and Discussion

This chapter will provide the results for the literature study and the believed suitability of the analysed batteries, as well as present the results of the case study provided by Vattenfall. In Figure 5.1, all of the batteries analysed are presented and how they compare between themselves. For this figure, **LFP** is used as representative of the **LIB** (for more specific values). Individual comparisons between the **LFP** and respective alternative can be found in the appendices, specifically Section A.1.

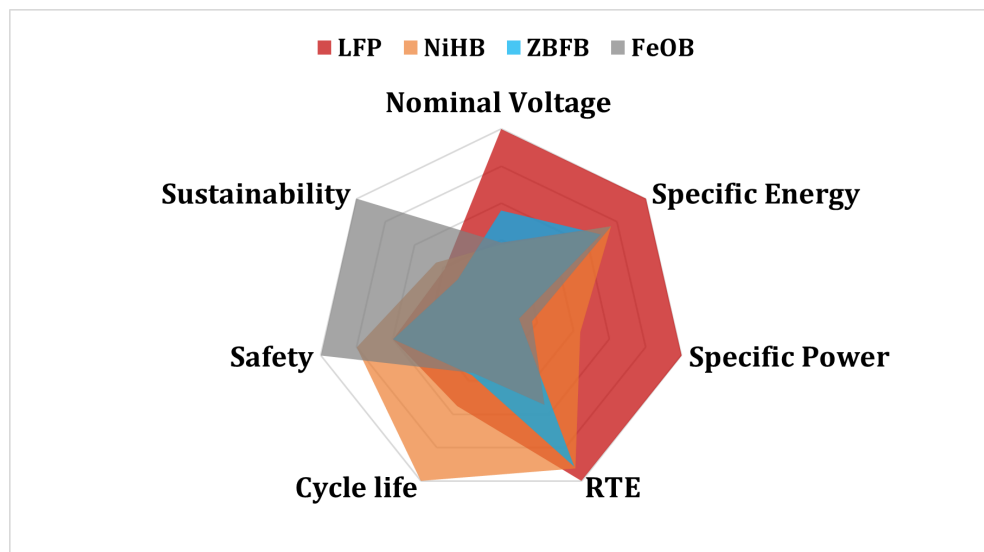


Figure 5.1: Radar graph of select parameters of all identified batteries in comparison to the Lithium Iron Phosphate battery (LFP). NiHB = Nickel-Hydrogen Battery, ZBFB = Zinc-Bromide Flow Battery and FeOB = Iron-Air Battery. **OBS:** the figure have been modified for sake of visibility, the real values are found in Appendices A.4.

What can be identified is that the **LFP** possess overall the best performance. However, in three of the categories it is not the best. For cycle life, the **NiHB** is much better while in sustainability and safety, the **FeOB** is more superior. The **ZBFB** unfortunately do not have any aspect shown that it is "best" in. However, not all aspects are considered here of course and it does have its own benefits, such as easier scalability from the disconnect between power and energy capability.

5.1 Suitability of Applications

The full list of the believed and described suitability of the **LIB** and the selected alternatives in Section 4.2.4 are presented in Table 5.1.

Table 5.1: Summary of technical suitability of the Nickel-Hydrogen Battery (NiHB), Zinc-Bromine Flow Battery (ZBFB) and Iron-Air Batteries (FeOB) when compared to the Lithium-ion Battery (LIB). "S" means suited, "=" indicates the battery to be equal to LIBs, while "+" and "-" indicates better or worse than, respectively. The "*" signifies important or relevant comments associated with the statement which can be read in the respective analysis section

	LIB	NiHB	ZBFB	FeOB
Load-Frequency Control Services (excl mFRR)	S*	=*	-	-
Voltage Control	S	-	-	-
Congestion Management	S*	=	=	=*
Black Start	S	-	-	-
Backup Power	S	-	-	-
Renewable Integration	S	=	=	=
Peak Shaving	S	=	=	=*
Energy Arbitrage	S	+	=	-
Local Flex Markets	S	-	-	-

As can be seen, for most applications the **LIB** is equal or more suited than the alternatives. It is only in one case where it is believed that an alternative is better than the **LIB**, namely the **NiHB** for energy arbitrage. However, all of this is based on the current performance of these technologies. Part of the aim is to investigate what changes are expected in the coming 5-10 years. Based on various sources from the literature review (and some additions), the improvements that are believed to be made by 2030 for each battery are presented in Table 5.2 and 5.3.

Table 5.2: Part 1 - Technical parameters now and in 2030 for the Lithium Iron Phosphate battery (LFP), Nickel-Hydrogen Battery (NiHB), Zinc-Bromide Flow Battery (ZBFB), and Iron-Air Battery (FeOB). RTE = Round-Trip Efficiency, and the "*" mark means that it is the targeted development, and not necessarily what will be achieved

		Specific Energy (Wh/kg)	Energy Density (Wh/L)	Specific Power (W/kg)	RTE	Lifetime	Sources
LFP	Now	90-120	197-433	4,000-10,000	92	5-20	[42, 11, 139]
	2030		200-600		94	8-30	
NiHB	Now	55-75	60	220	85	30	[43, 24, 93]
	2030	75+			85-90		
ZBFB	Now	60-85	15-70	n.a	75	5-20	[104, 103, 11, 43]
	2030				67-95	9-30+	
FeOB	Now	65-92.5	n.a	20-150	50	n.a	[113, 118, 140]
	2030				80*		

Table 5.3: Part 2 - Technical parameters now and in 2030 for the Lithium Iron Phosphate battery (LFP), Nickel-Hydrogen Battery (NiHB), Zinc-Bromide Flow Battery (ZBFB), and Iron-Air Battery (FeOB). The "*" mark means that it is the targeted development, and not necessarily what will be achieved

		Cycle life	Self-discharge	Discharge duration	Capital cost (per kWh)	Capital cost (per kW)	Sources
LFP	Now	3,000-8,000	<1%/month	1min-8h	\$232-599	\$33-250	[42, 48, 11] [139, 43]
	2030	4,500-15,000			\$80-340		
NiHB	Now	30,000	40%/month	hours	\$330	\$165	[43, 24]
	2030		<40%/month				
ZBFB	Now	3,650-10,000	1-2.3%/hr	8-10hrs	\$325-1068	0-890	[43, 11] [107, 24]
	2030	10,000+			\$108-576		
FeOB	Now	2750	1,71%/d	up to 100h	\$25	n.a	[113, 118, 125] [130, 141]
	2030		0.1%/day*				

For the **LFP**, the notable improvements are for its lifetime and a slightly higher **RTE**. In the case of **NiHB** it is expected to see some small improvements, notable its **RTE** is expected to increase and that its self-discharge will decrease, which is a pain point currently. Following is the **ZBFB**, of which the literature indicates that it will increase its **RTE**, cycle life and lifetime as well as lower cost of energy. However, the core issues of high self-discharge and its weekly constraint is not believed to be lessened, which means that there is less of an impact on the outcome from its development. It is also still worse in most categories compared to the **LFP**. Lastly, the **FeOB** is mostly unknown how it will develop. However, some sources have stated their targets for what they want to achieve, which notable is a higher **RTE** and less self-discharge, both things that are major drawbacks of this battery. Therefore if achieved, this makes a large difference to what the technology is capable of.

Combining all of this knowledge, it is possible to update Table 5.1 with how it will look by 2030. This is shown in Table 5.4. As can be observed, both the NiHB and FeOB see changes to their suitability, which are mostly because of lower self-discharge, which opens up for applications with intermediate storage duration, and in the case of the FeOB an increased efficiency in line with other batteries. The ZBFB unfortunately is not believed to change its situation when compared to the LFP, since its pain points stay mostly the same. However, it still has the benefit of a more abundant material which means that at least for the applications where it is equally suited, it can still be used as an alternative if lithium shortage is an issue.

Table 5.4: Summary of technical suitability of the Nickel-Hydrogen Battery (NiHB), Zinc-Bromine Flow Battery (ZBFB) and Iron-Air Batteries (FeOB) when compared to the Lithium-ion Battery (LIB) in 2030. "S" means suited, "=" indicates the battery to be equal to LIBs, while "+" and "-" indicates better or worse than, respectively. The parts that are highlighted have changed from the previous table

	LIB	NiHB	ZBFB	FeOB
Load-Frequency Control Services (excl mFRR)	S	=	-	-
Voltage Control	S	-	-	-
Congestion Management	S	=	=	=
Black Start	S	-	-	-
Backup Power	S	-	-	-
Renewable Integration	S	+	=	+
Peak Shaving	S	+	=	=
Energy Arbitrage	S	+	=	=
Local Flex Markets	S	=	-	-

The last question then is whether it is believed if any of the alternatives identified can compete with the LIB. The short answer is that it is only the NiHB that is believed to be suitable, but only in some instances. However, its long-term competitiveness is hard to say, and if its development heads towards utilising more cobalt, its sustainable benefit will diminish. It is also debatable whether it is a good idea to suggest a battery utilising a metal (Nickel) that has growing concerns surrounding its availability. Especially when the original problem was that there is not enough lithium. However, alternatives are always welcomed, and at least according to an representative from Schlumberger/Enervenue, it was stated that they believe they have stable enough supply lines of nickel in the foreseeable future [93]. They also believe that nickel used per battery will decrease, which mitigates the issue at least a

little.

In the case of the **ZBFB**, it is believed that its current competitiveness is not really high enough. Even worse, its development in the near future is believed to be too small to also make it "catch-up" to the **LIB**, if not for some unforeseen incredible discovery. However, it does possess the benefit of not using lithium, which could prove to be even more important in the future. Although, the same goes for the other two chemistries looked at.

Lastly, the **FeOB** is at the moment not a proper alternative based on the available literature. However, its potential is very high, and it has the best opportunity to really be a more sustainable and cheap option in contrast to a **LIB**, even if performance wise it lacks. It especially has a clear unique selling point being the only battery capable of up to 100 hours of discharge. Although, only time will tell how it actually develops.

5.2 Off-shore Wind Park Case

Based on the methodology and given parameters from 4.3, the techno-economic specifications of the battery can be calculated, and are shown in Table 5.5. The OPEX, the energy that is lost through discharge and the total energy going into the battery annually is shown in Table 5.6.

Table 5.5: Lifetime techno-economic specifications

	Unit	LFP	NiHB
Weight	kg	2381	2778
Required Capacity	MWh	312	258
Total Degradation	MWh	81	26
Rated Capacity	MWh	393	284
CAPEX	M€	104	79

Table 5.6: Yearly specifications

	Unit	LFP	NiHB
OPEX	M€	0.915	0.661
Self-Discharge	MWh	43	1234
Energy in per year	MWh	20423	23293

With this knowledge, it is possible to perform a discontinuity calculation, which yearly result is found in the Appendices Section A.2. Otherwise, Figure 5.2 shows the yearly net-present-cost.

The final result is shown in 5.7, which shows how NiHB has the lower LCOS for this case, with €515/MWh in contrast to €785/MWh for the LFP. This is somewhat expected, as other studies performed by other authors on similar cases got the same result [43, 136], although not the same LCOS value of course. It is also somewhat in-line with the LCOS analysis performed by Lazard in 2021 [142], which state that for a transmission and distribution use-case (of which this use-case is applicable) with around 10MW/60MWh, its LCOS should be around €1364-2566 per MWh, which is much higher than for the NiHB. However, the Lazard case used 25 cycles per year, which if also applied for the off-shore case, would put the LCOS of the LFP at €2951/MWh and the NiHB at €1857/MWh, which is in the same range or slightly above it.

Notably, the cycle life for both batteries are plenty enough to cover the whole project lifetime. However, the suggested lifetime of a LFP is only 15 years, meaning that it has to be replaced once during the project lifetime, as can be identified in 5.2. This has a significant impact on the result, as even

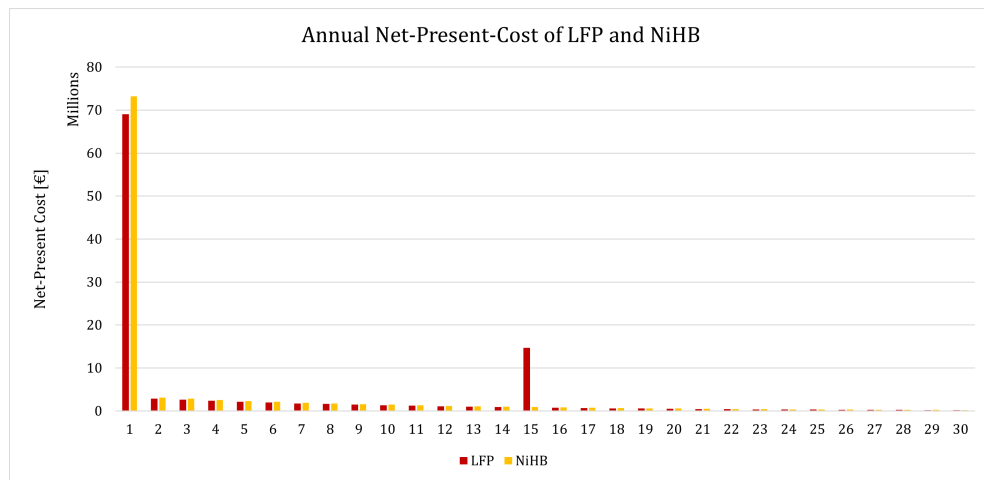


Figure 5.2: Annual Net-Present-Cost of Lithium Iron Phosphate (LFP) and Nickel-Hydrogen (NiHB) battery over the projects 30 year lifetime.

Table 5.7: The Levelised Cost of Storage, based on the total lifetime energy output and cost for both Lithium Iron Phosphate (LFP) and Nickel-Hydrogen (NiHB) battery.

	Unit	LFP	NiHB
Total Net-Present Cost	M€	153	100
Total Energy produced	MWh	18750	18750
LCOS	€/MWh	785	515

though the electricity demand for the **NiHB** per year is much higher because of self-discharge, it is still less expensive overall. It was also found that even if the lifetime of a **LFP** would be 30 years, because of degradation it would still not be less expensive. This means that the overbuild strategy probably has a large influence on the outcome of this study. Another study should probably be performed where a different strategy is utilised to see if the outcome is different. Something else that also has a large influence on the **LCOS** is that half of the cycles performed are only half-load. If it was only full load cycles, that would put the **LFP** and **NiHB** at €725 and €472 per MWh respectively.

Chapter 6

Conclusions and Future work

In this last chapter, the final conclusion of this work will be discussed, as well as some reflections from the author where this work fits in the larger part of this field and what should be further looked at or be picked up instead.

6.1 Conclusions

The use of large-scale **BESS** to combat intermittent power production and instability in the grid is only going to grow. As one of the most mature and performance wise strongest batteries today, the **LIB** will be at the forefront of usage. But the growing shortage of lithium as well as safety risks and questionable use of cobalt, means other alternatives are needed. This is where the **NiHB** is believed to be well suited as an alternative. as it is a very durable and safe battery, with an impressive cycle life, system lifetime and durability. Moreover, its low degradation was essential for why it was the better choice for the Offshore case, even though it cost more per watt or watt-hour. However, a key discussion point is that nickel has come under question for if we have enough – or rather if the supply can keep up with the growing demand of this metal. Circling back to the main problem, which was the issue of lithium availability, the question then is really whether it is then good to suggest an alternative that also has a potential availability issue in the future. However, nickel is in a much better spot than lithium, and it is not the idea to suggest that **NiHB** should be used for everything. The point is for it to be used for applications where it really is better than other alternatives. Overall, the net-outcome is still positive. In the case of the **ZBFB**, its performance is good but not at a point where it can really be considered a good alternative to **LIB**, except in the cases where you really want a non-lithium battery. But in those

situations, why not just use the **NiHB** instead? Moreover, its constrain of a full discharge each week limits its ability for many applications, if that is not mitigated then its hard to see it being used much in the future. Lastly, the **FeOB** has great potential, with its unique aspects such as the very high discharge duration as well as super safe and abundant material which it uses. Its current performance is subpar, but it has a lot of room to grow and hopefully, even though its development is hard to say, with companies such as Form Energy and a potential renewed interest in the technology, many things can happen. However, the conclusion should still be that at the moment its not a good alternative. But it is suggested that one should revisit the technology at a later stage, after it has developed more. Overall though, the firm grip that the **LIB** have on the market is believed to continue, although less and less with time as new technology gets developed and improved upon, that could replace it for applications where it is not needed. There might even be completely new technologies, not at all mentioned here and maybe completely unknown today, that show to be a great alternative for large-scale energy storage.

6.2 Future work

As this work can be viewed as a preliminary investigation for what batteries to look out for to use for large-scale application, it is the belief of this author that more studies can be performed on the subject of iron-air batteries, to see how it performs on large scale and how it will develop, and not just in the lab. The same goes for the nickel-hydrogen battery, except focus should more be on real life demonstration and commercial projects to verify its suitability even more. There is also room for improvement for both batteries especially on self-discharge, which is a major drawback for the two. For the zinc-bromide battery, research for how to minimise the need for a weekly full discharge and shunting could open more avenues of usability. Moreover, sodium-ion batteries was not investigated deeper than in the literature study. It is believed that this technology also have large potential and should definitely be a focus of another study. Regarding the case study, the choice of using an overbuild strategy to compensate for degradation is believed to have a large influence on the outcome of the study. As mentioned already, it is therefore in interest to try other strategies to compensate for degradation, such as augmentation.

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Appendix A

Supporting materials

A.1 Individual Radar Graphs

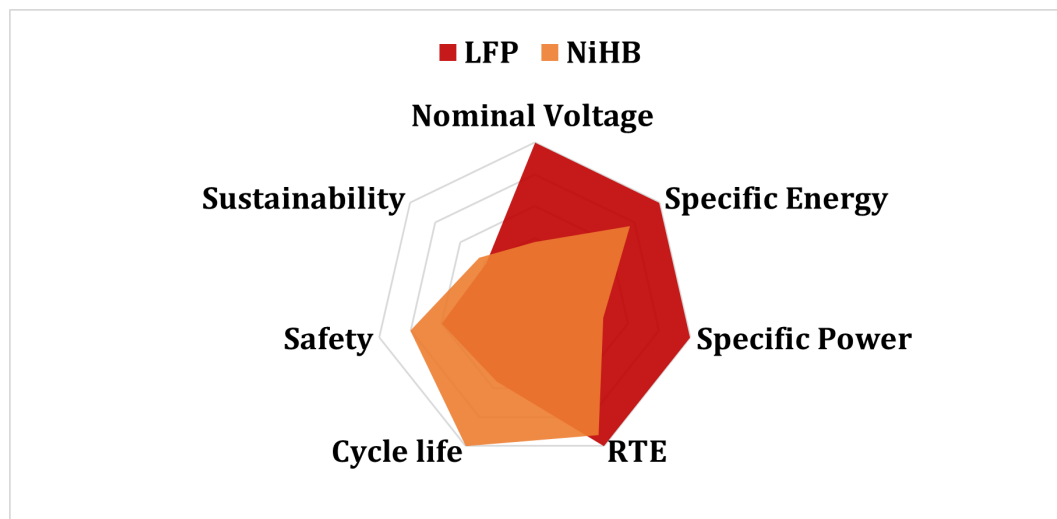


Figure A.1: Radar graph for select parameters of the Lithium Iron Phosphate (LFP) and Nickel-Hydrogen Battery (NiHB). **OBS:** the figure have been modified for sake of visibility, the real values are found in Appendices [A.4](#).

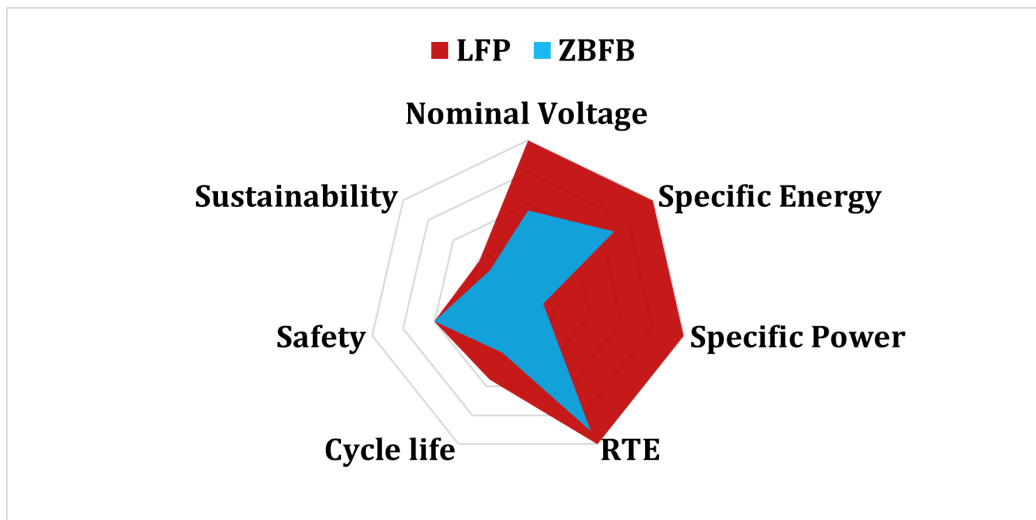


Figure A.2: Radar graph for select parameters of the Lithium Iron Phosphate (LFP) and Zinc-Bromide Flow Battery (ZBFB). **OBS:** the figure have been modified for sake of visibility, the real values are found in Appendices A.4.

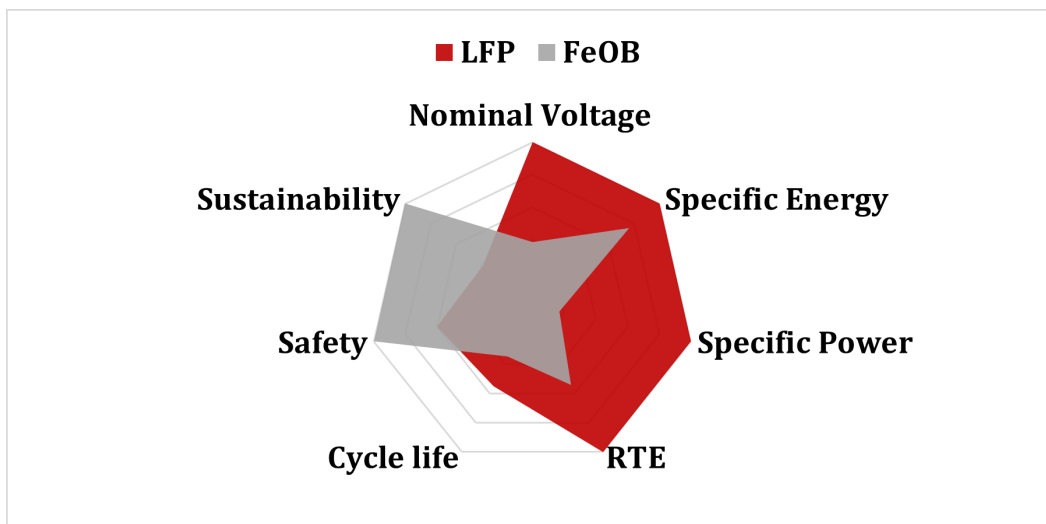


Figure A.3: Radar graph for select parameters of the Lithium Iron Phosphate (LFP) and Iron-Air Battery (FeOB). **OBS:** the figure have been modified for sake of visibility, the real values are found in Appendices A.4.

A.2 Offshore Wind park case

Table A.1: Discontinuity calculation per year for both Lithium Iron Phosphate (LFP) and Nickel-Hydrogen (NiHB) battery over the projects lifetime, where i = discontinuity factor.

Year	i	LFP	NiHB
1	1	105697127	81283316
2	0.90909	1906437	1826532
3	0.82645	1733124	1660483
4	0.75131	1575568	1509530
5	0.68301	1432334	1372300
6	0.62092	1302122	1247546
7	0.56447	1183747	1134132
8	0.51316	1076134	1031030
9	0.46651	978304	937300
10	0.4241	889367	852091
11	0.38554	808515	774628
12	0.35049	735014	704207
13	0.31863	668195	640188
14	0.28966	607450	581989
15	0.26333	27833357	529081
16	0.23939	502024	480983
17	0.21763	456386	437257
18	0.19784	414896	397507
19	0.17986	377178	361370
20	0.16351	342889	328518
21	0.14864	311718	298653
22	0.13513	283380	271502
23	0.12285	257618	246820
24	0.11168	234198	224382
25	0.10153	212907	203984
26	0.0923	193552	185440
27	0.08391	175956	168582
28	0.07628	159960	153256
29	0.06934	145419	139324
30	0.06304	132199	126658

A.3 Calculation of environmental impact for Nickel-Hydrogen battery

Table A.2: Parameters for Nickel that are used in the calculations. GWP = Global Warming Impact, CED = Cumulative Energy Demand

GWP	CED	Molar Mass
13	236	58.69
CO ₂ kg	MJ/kg	g/mol

Table A.3: Mass of battery components from experiment [92]. Where CC = Current Collector

	Total Mass	Partial Ni Mass	Ni Mass Percentage
Ni(OH)₂	3.27g	2.07g	63.3%
NiCoMo	0.57g	0.15664g	27.5%
CC. Nickel Foam	1.36g	1.36g	100%
Seperator	0.072g	-	-
Electrolyte KOH	0.4g	-	-
Total	5.672	3.58671g	63.2%

$$M_{\text{Ni(OH)}_2} = M_{\text{Ni}} + 2M_{\text{O}} + 2M_{\text{H}} = 58.69 + 32 + 2.02 = 92.71$$

$$m_{\text{Ni}} = \frac{m_{\text{Ni(OH)}_2}}{M_{\text{Ni(OH)}_2}} * M_{\text{Ni}} = \frac{3.27}{92.71} * 58.69 = 2.07 \quad (\text{A.1})$$

$$M_{\text{NiMoCo}} = M_{\text{Ni}} + M_{\text{Mo}} + M_{\text{Co}} = 58.69 + 95.95 + 58.933 = 213.573$$

$$m_{\text{Ni}} = \frac{m_{\text{NiMoCo}}}{M_{\text{NiMoCo}}} * M_{\text{Ni}} = \frac{0.57}{213.573} * 58.69 = 0.15664 \quad (\text{A.2})$$

The conclusion is therefore that for a **NiHB**, its **GWP** and **CED** are equal to 63.2% of the original value for pure nickel.

A.4 Material sustainability of studied batteries

In Table A.4 below, the values used for the radar graphs as shown in the results are presented. The "Sustainability" category is the average of the three last rows in the table (normalised). For the qualitative scale of 1-5, the choice of each value was decided upon what was found in the literature review in general. In some cases, the values were modified for sake of visibility in the radar graphs, such as the specific power of ZBFB, which was not available as a value, but not strictly 0 as otherwise would have been shown in the figure. Therefore, the figures should not be taken as exact, instead the values below are a more proper indication.

Table A.4: Values used for radar graphs for each battery studied, namely LFP = Lithium Iron Phosphate, NiHB = Nickel-Hydrogen, ZBFB = Zinc-Bromide Flow, FeOB = Iron-Air. For the qualitative scale, 1 = worst and 5 = best.

	Unit	LFP	NiHB	ZBFB	FeOB
Nominal Voltage	V	3,3	1.25	1.85	1.28
Specific Energy	Wh/kg	105	80	72.5	80
Specific Power	W/kg	500	220	-	85
RTE	%	92	85	84	50
Cycle life	amount	5,500	30,000	3,650	2750
Safety	1-5	3	4	3	5
Material	1-5	2	3	3	4
Cumulative Energy Demand	MJ per Wh	0.97	1.87	1.99	0.31
Global Warming Potential	kgCO ₂ -eq per Wh	0.161	0.103	0.158	0.0174

