POLITECNICO DI TORINO

Collegio di Ingegneria Energetica

Corso di Laurea Magistrale in Ingegneria Energetica e Nucleare

EIT InnoEnergy Master in Energy Storage

Tesi di Laurea Magistrale

Techno-economic Assessment on Flow Batteries for the Industrial Sector in Spain

Relatori

Prof. Daniele MARCHISIO
Prof. Cristina PRIETO
Prof. Alda SIMÕES

Candidata

María Dolores GUERRERO GARRIDO

July 2024

This thesis is written as the final portion of the Master's Programme in Energy Storage, a double degree programme organised by EIT InnoEnergy in collaboration with Politecnico di Torino and Instituto Superior Técnico.

This thesis is supervised by both universities in conjunction with Build to Zero S.L., who proposed the topic and research support throughout the process.

TÉCNICO LISBOA

Politecnico di Torino
1859

eit InnoEnergy

Co-funded by the European Union

BUILD TO ZERO

Abstract

In the context of decarbonisation, climate change adaptation, and security of supply, industry decarbonisation is one of the main concerns in the European Union affecting the industrial sector development. Despite the sector acknowledges this fact, the wide range of technologies and their rapid development are some of the barriers that need to be overcome in order to achieve the policy, societal, and industrial owners' targets.

As the demand for decarbonisation intensifies across economic sectors and renewable energy gains prominence, the development of energy storage technologies is crucial to achieve high shares. However, the diversity of industry requirements is a challenge, particularly in sectors where capacity holds paramount importance. In addressing this niche, flow batteries are one of the most promising technologies, bridging the gap closed and open energy storage systems.

Considering the high renewable share in Spain, this research critically evaluates the viability of flow batteries as a strategic decarbonisation product for the industrial sector in Spain. Through a comprehensive techno-economic analysis, the agents that may either impede or accelerate the technology's integration are identified such as optimal load profiles, conditions for adoption and strategic market considerations. The outcome provides a nuanced understanding, guiding industries towards informed decision-making in the evolving energy landscape.

Key words

Industrial decarbonisation, redox flow batteries, vanadium, energy storage, heat decarbonisation, industrial electrification.

Table of Contents

List of Figures

List of Tables

Glossary of abbreviations and acronyms

AC	Alternating Current
AI	Artificial Intelligence
BMS	Battery Management System
BTM	Behind-The-Meter
CAES	Compressed Air Energy Storage
CAPEX	Capital Expenditures
CCUS	Carbon Capture Use and Storage
CF	Capacity Factor
CFD	Computational Fluid Dynamics
CRM	Critical Raw Material
CRMA	Critical Raw Materials Act
CSP	Concentrated Solar Power
DAC	Direct Air Capture
DC	Direct Current
EASE	European Association for Energy Storage

EDLC	Electric Double Layer Capacitor
EMS	Energy Management System
EOL	End-of-Life
ESW	Electrochemical Stability Window
ETES	Electrothermal Energy Storage
EU	European Union
EV	Electric Vehicle
FTM	Front-The-Meter
GHG	Greenhouse gas
HTHP	High Temperature Heat Pump
IDAE	Spanish Institute of Energy Savings and Diversification
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
IPPU	Industrial Processes and Product Use
IRA	Inflation Reduction Act
KPI	Key Performance Indicator
LCA	Life Cycle Assessment
LCOE	Levelized Cost of Energy
LCOS	Levelized Cost of Storage
LDES	Long Duration Energy Storage
LIBs	Lithium-ion Batteries
LULUCF	Land Use, Land Use Change and Forestry
MECE	Mutually Exclusive Collectively Exhaustive
NaS	Sodium-Sulphur Battery
NASA	National Aeronautics and Space Administration
NECP (*PNIEC*)	Spanish Integrated National Energy and Climate Plan (*Plan Nacional Integrado de Energía y Clima*)
NZE	Net Zero Emissions
NZIA	Net Zero Industry Act
O&M	Operation & Maintenance
OCV	Open Circuit Voltage

OPEX	Operational Expenditures
P2H	Power to heat
P2P	Power to power
PbA	Lead-acid Battery
PCM	Phase Change Materials
PEM	Proton Exchange Membrane
PHES	Pumped Hydro Energy Storage
PPA	Power Purchase Agreement
PV	Photovoltaic
RFB	Redox Flow Batteries
SAF	Sustainable Aviation Fuel
SC	Super Capacitor
SDGs	Sustainable Development Goals
SMES	Superconducting Magnetic Energy Storage
SMR	Steam Methane Reforming
SOC	State of Charge
SPERT (*PERTE*)	Strategic Project for Economic Recovery and Transformation (*Proyectos Estratégicos para la Recuperación y Transformación Económica*)
SRIA	Strategic Research and Innovation Agenda
TES	Thermal Energy Storage
TLCC	Total Life-Cycle Cost
TRL	Technology Readiness Level
TSO	Transport System Operator
UN	United Nations
UTES	Underground Thermal Energy Storage
VRE	Variable Renewable Energy
VRFB	Vanadium redox flow battery
WACC	Weighted Average Cost of Capital
WTTES	Water Tank Thermal Energy Storage
ZBFB	Zinc-bromine flow battery

Glossary of units and symbols

a_i	Activity of species i
A	Ampere, unit of current
bar	Bar, unit of pressure
i_{cell}	Cell current density
ºC	Celsius degree, unit of temperature
c_i	Concentration of species i
C_i	Cost of component i
C	Coulomb, unit of charge
cm^3	Cubic centimeters, unit of volume
m^3	Cubic meter, unit of volume
I	Current
i	Current density
ρ	Density
A_{cell}	Effective cell area
η	Efficiency
I_0	Equilibrium current
€	Euro, monetary unit
F	Faraday's constant, 96 485 C/mol
Q	Flow rate
$\Delta\bar{g}_{reaction}$	Free Gibbs molar variation
GWh	Giga Watt-hour, unit of energy
GW	Gigawatt, unit of power
g	Gram, unit of mass
h	Hour, unit of time
R	Ideal Gas Constant, 8.134 J/mol-K
kg CO_2 eq.	Kilogram of equivalent CO_2, global warming potential unit.
kg	Kilogram, unit of mass
kton	Kiloton, unit of mass
kWh	Kilowatt hour, unit of energy

kW	Kilowatt, unit of power
MJ	Mega Jule, unit of energy
MW_{th}	Mega Watt thermal, unit of thermal power
MWh	Megawatt hour, unit of energy
MW	Megawatt, unit of power
m	Meters, unit of length
mW	Miliwatts, unit of power
M€	Millions of euros, monetary unit
M	Molarity, unit of concentration in solution
mol	Moles, unit of quantity
E	Nernst Potential
N_{cell}	Number of cells
z_F	Number of electrons transferred in a reaction
n_{RDS}	Number of electrons transferred in the rate determining step
η_i	Overvoltage associated to phenomenon or element i
%	Percentage
lb	Pounds, unit of mass
$\dot{W}$	Power
k	Reaction rate
s	Seconds, unit of time
cm^2	Square centimeters, unit of area
m^2	Square meter, unit of area
E_i^θ	Standard Nernst Potential in element i
ν_i	Stoichiometric coefficient of species i
β	Symmetry factor
TWh	Tera Watt-hour, unit of energy
t	time
ton	Ton, unit of mass
c_i	Unitary cost of component i
USD	United States Dollars, monetary unit

ν	Viscosity
V	Volts, unit of voltage
Wh	Watt hour, unit of energy
Wh/kg	Watt-hour per kilogram, unit of gravimetric energy density
Wh/L	Watt-hour per litter, unit of volumetric energy density

1. Introduction

The energy sector faces a moment of high geopolitical tensions and uncertainty, marked by the security of supply concerns and price volatility affecting critical value chains globally. This challenging landscape is exacerbated by the urgent need to address the imminent climate crisis, which require an all-encompassing solution that can seize the multiple dimensions of the problem

1.1. Decarbonisation needs

Over recent decades, the need for decarbonisation has raised increased interest, spurred by the scientifically established correlation between climate change and greenhouse gas (GHG) emissions. Scientific consensus unequivocally attributes climate change to anthropogenic emissions, stemming from human activities (Figure 1) [2]. These emissions have elevated GHG concentrations in the atmosphere, encompassing carbon dioxide, natural gas, and nitrous oxide, among others. This concentration disrupts both mass and energy balances, exerting profound impacts on the global climate [3].

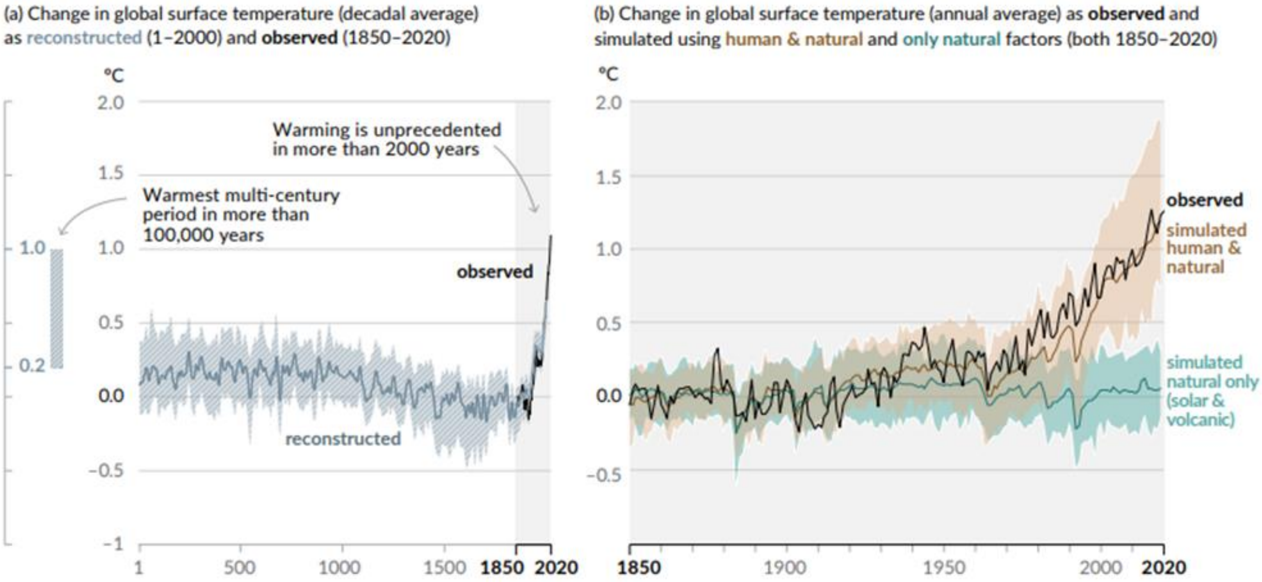


Figure 1. Changes in global Surface temperature relative to 1850-1900. [2]

Global warming due to the greenhouse effect represents one of the most widely recognised negative consequences of climate change. The disturbance in the carbon cycle is closely intertwined with global warming, amplifying the participative medium effect of atmospheric air in terms of heat transfer. Carbon dioxide alters atmospheric radiation properties, enhancing heat retention and exacerbating the greenhouse effect, thereby warming the planet by retaining heat in the global surface. While GHGs have historically influenced global temperature cyclically, the accelerated rise in their concentrations has introduced unprecedented uncertainties in climate behaviour under the fast change of circumstances. Among others, effects on natural carbon sinks given the higher concentration absorbed are another rising concern, such as acidification of oceans, with far-reaching environmental repercussions [4].

Although carbon dioxide is not the only greenhouse gas, it serves as a reference due to its significant influence on Earth's temperature and its long-term prevalence. Its molecular stability, compared to other greenhouse gases like methane, underscores its centrality in climate dynamics [4]. The release of these gases is highly linked with energy consumption and economic growth, rendering emissions reduction a formidable challenge within the prevailing business-as-usual paradigm. The latest Intergovernmental Panel on Climate Change (IPCC) report underlines a concerning trend of increasing GHGs emissions, particularly attributed to fossil fuels and industrial activities [3].

Experts conclude that the time window to prevent climate change has largely closed, requiring a shift from solely focusing on mitigation to a combined approach incorporating adaptation strategies [5]. The climate emergency cascades into interconnected challenges associated with climate itself, but also biodiversity loss, poverty, and public health concerns unequally distributed geographically [6]. This imperative for action finds expression in the 2030 Agenda for Sustainable Development adopted by all United Nations (UN) Member States in 2015. At its core, this agenda outlines 17 Sustainable Development Goals (SDGs) that serve as a rallying call for global urgent action, involving climate emergency and interdependent negative effects of current development models [7].

Addressing the adverse effects of climate change demands a global action towards GHGs emissions shift through all the economic sectors. The complexity of the problem stems from the global consequences of local actions, emphasizing the need for impactful innovation tailored to specific environmental contexts. There is not a fit-for-all approach or solution when it comes to climate change mitigation and adaptation, requiring the formulation of strategic community and technology development roadmaps that better align with local environmental constraints and resources [5].

The European Union (EU) is a pioneer in decarbonisation policies and efforts, with an ambitious target to achieve carbon neutrality by 2050, spearheaded by initiatives like the Fit-for-55 package [8]. The main objective of this package is to enable the legislative framework required to reduce the carbon emissions by 55% in the EU by 2030, shaping the path towards carbon neutrality at a faster pace.

A pivotal objective of the union is to guarantee the security of energy supply by reducing dependence on imports. In 2022, due to the limited fossil fuels reserves, the EU produced around 37,5% of the energy used domestically, while importing the remaining 62,5% [9]. The energy dependence level varies among member countries [10] and is intricately tied to the energy consumption ratio and the availability of reserves, including renewable energy sources (Figure 2).

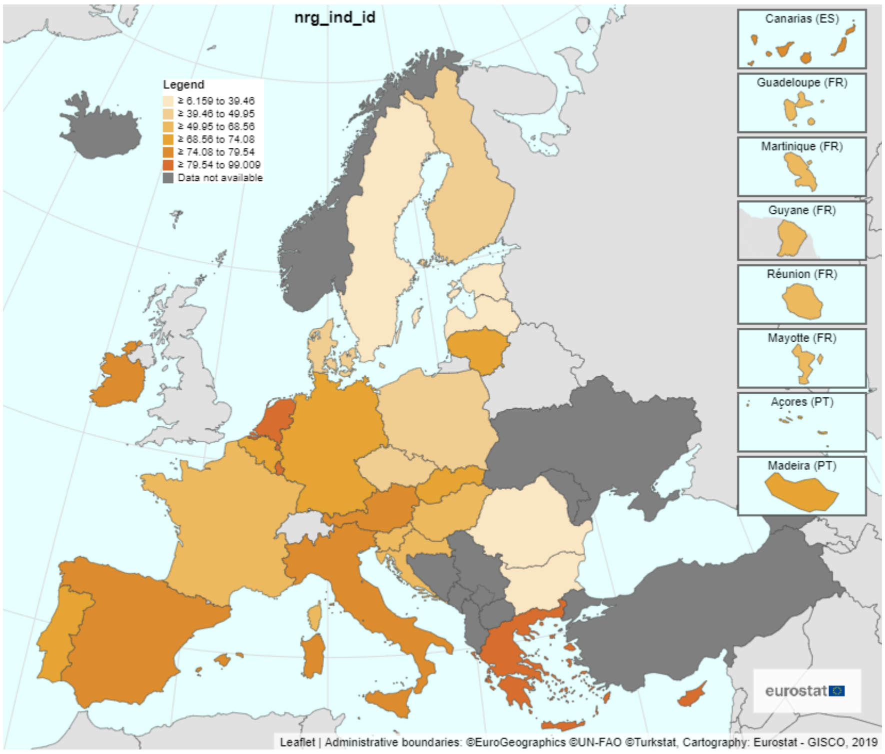


Figure 2. Energy imports dependency in the European Union country members in 2022. [10]

Under these goals, the REPowerEU agenda has been implemented accompanied by a financing mechanism designed to bolster energy security of supply, decarbonisation, and environmental strategies. This plan was launched in May 2022, as a response to the Ukrainian Invasion and gas market anomalies, which supposed a pivotal change of the energy supply and transition EU plans that consider gas as the main transition energy vector. Key initiatives include enhancing energy efficiency in order to curtail energy consumption, diversifying energy imports, accelerating the deployment of renewable energy generators and reducing fossil fuel usage in industry and transportation. Smartly combination of investment and reforms should provide the resources required to fasten up the clean transition and spur innovation at the predetermined pace [11].

An important factor to consider in the accomplishment of the REPowerEU agenda and Fit-for-55 ambitions is the reliance on other materials and manufacturing capabilities. While addressing energy dependence, it is imperative to avert a transfer of dependency to strategic supply chains crucial for economic resilience, such as those underpinning clean technologies manufacturing and critical materials for the energy transition and digitalisation. In order to diminish these challenges, the EU has recently enacted the Net-Zero Industry Act (NZIA) [12] and the Critical Raw Materials Act (CRMA) [13], laying the groundwork for the development of strategic value chains. It is worth noting the importance of both acts in order to fulfil the ambitious targets set, particularly in the global competition for investment, where the United States Inflation Reduction Act (IRA) emerges as a strong contender [14].

Mainly driven by the fluctuations in fossil fuel prices, declining costs of variable renewable energy sources, and evolving regulatory frameworks, the energy transition is not merely imperative, but also economically advantageous. This is a momentum to invest in clean energy technologies and drive innovation in the sector. The main barrier to overcome is the decision on which technology fits best the application considered and the financial strategies to maximize the societal and economic benefits.

1.2. Industrial Sector Decarbonisation

As previously discussed, the energy sector plays a crucial role in societal development, with its cross-sectorial dimension impacting heavily on diverse economic sectors. Similarly, the industrial sector presents comparable challenges in the economic and sustainable development. Society heavily relies on the consumption of goods and products, spanning industries such as food industry, chemicals, and other important value chains. To enhance a community resilience, the industrial sector aligns with the consumption patterns of the community it serves and quality standards.

Simultaneously, the industrial sector stands as one of the primary sources of CO_2 globally accounting for over 40% of global emissions, alongside the transportation and residential sectors (Figure 3), a trend mirrored in Europe and Spain (Figure 4). It is worth highlighting that over half of industrial emissions are associated with electricity and heat generation. This dichotomy underscores the urgency of decarbonising industry while preserving market competitiveness. Policies must be crafted to synchronize with the global market, offering cost-competitive solutions that facilitate a just transition and mitigate the risk of industry relocation, often referred to as *'Carbon leakage'* [15].

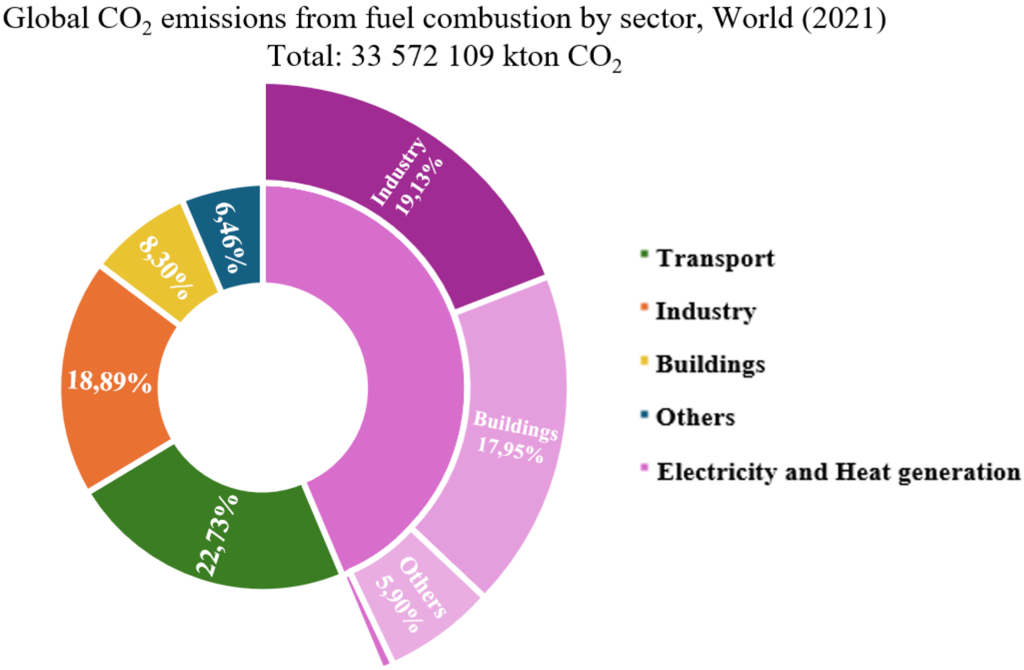


Figure 3. Global CO_2 emissions from fuel combustion by sector in the World (2021). Own calculations based on IEA data [16].

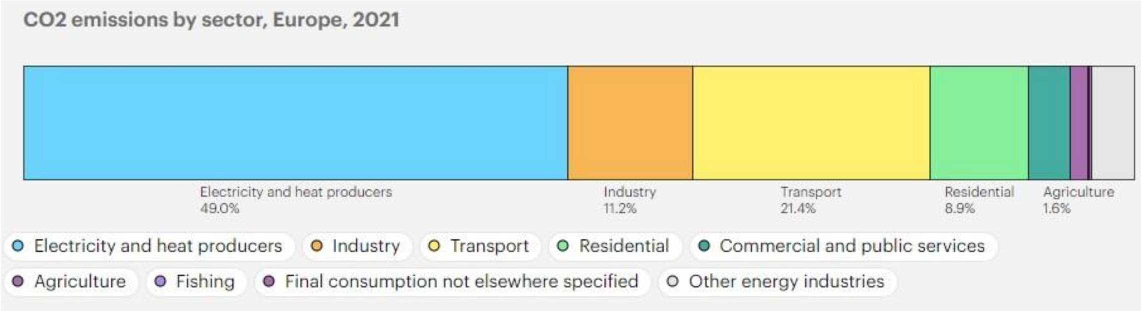


Figure 4. CO_2 emission by sector, Europe (2021). [17]

Depending on the process, type, and quantity of the good produced, both the energy demand profiles, and CO_2 emissions differ from one installation to other. It is crucial to consider both material and energy inputs in industrial processes to ascertain their carbon footprint. The carbon footprint of material refining and obtention should be considered, as well as the emissions associated with the energy generation. The former is commonly termed "process emissions", whereas the latter are referred to as "energy emissions" [18]. Emissions in organisations are often categorized into 3 scopes (Figure 5). Scope one encompasses direct emissions, originated by the company itself, including the process emissions. The second scope is referred to the indirect emissions for energy purchased as a utility. The third one accounts for indirect emissions generated by the consumer throughout the product's lifecycle [19], which is used to boost more carbon efficient products even far from the industry battery limits [20].

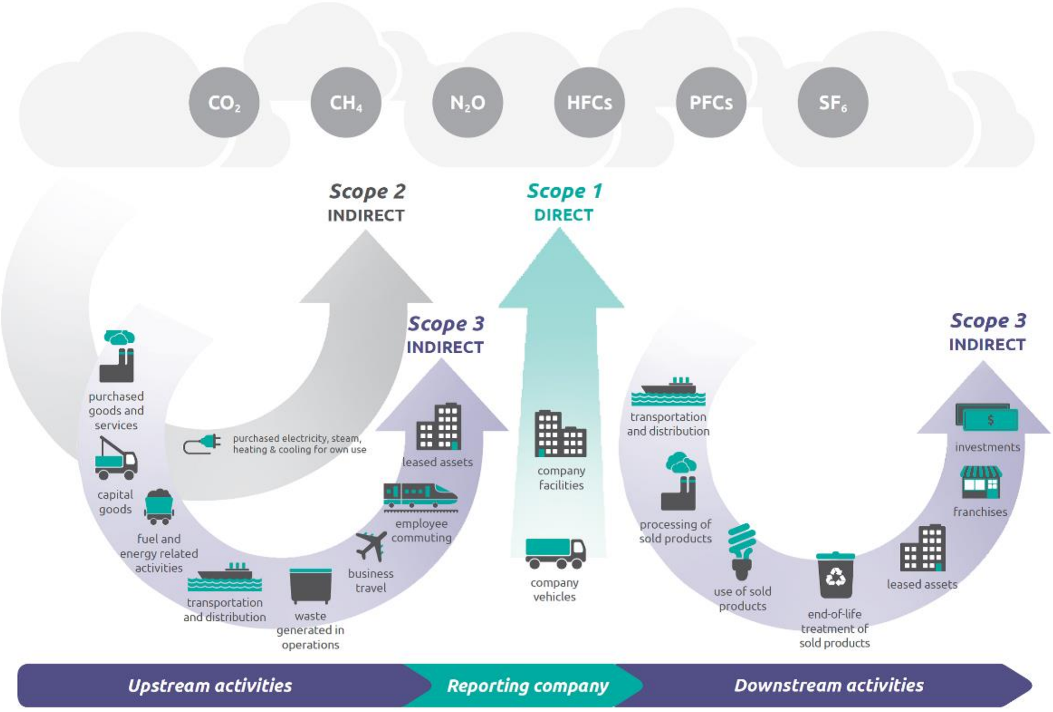


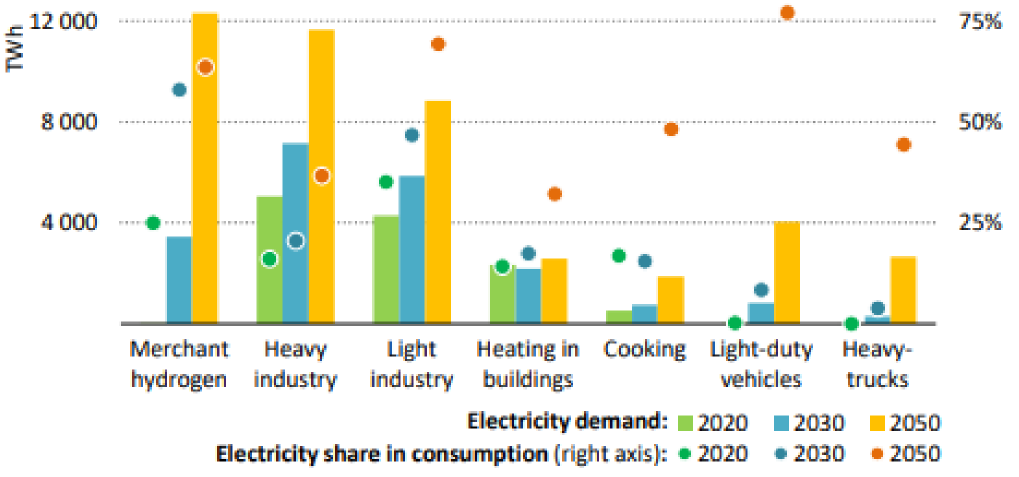
Figure 5. Organisational emission scopes exemplification scheme. [20]

The primary focus of this project will be on the energy supply shift, relative to the first and second scopes, where the company is less restricted to act and the impact on emissions abatement is high. However, the relative significance of each scope may vary depending on the industry and company type under consideration, and thus, addressing an organisation decarbonisation by switching the energy supply may not always be the first problem to tackle. For instance, in industries such as fertilisers production, where a substantial portion of ammonia production relies on fossil fuels [21], or in car manufacturing, where emissions associated with the product life (the third scope) generally outweigh the first and second scopes [22].

While industrial decarbonisation is technically feasible, achieving set goals required additional efforts [23]. As mentioned earlier, matching applications and decarbonisation solutions is not an easy task given the diversity of energy and mass profiles in industry. Therefore, a comprehensive integration studies are essential to consider both process requirements and local and regional constraints.

1.3. Renewable Electrification and Energy Storage

The primary strategy for decarbonising the European Union centres on the parallel electrification of the energy economy, while decarbonising the power sector [1]. This strategy is also highlighted by the International Energy Agency (IEA) as one of the most important drivers of emissions reductions in the Net Zero Emissions (NZE) scenario. The global expected electricity demand is expected to double between 2020 and 2050 under these conditions, mainly driven by the increase of more than 11 000 TWh increase in industry. Much of this volume is associated with the electrification of low- and medium-temperature heat, as well as secondary scrap-based steel production (Figure 6) [24].



IEA. All rights reserved.

Figure 6. Global electricity demand and electricity share in energy consumption in selected applications in the NZE scenario. [24]

Regarding the electrification of the industrial sector, different energy demand profiles must be considered. Industrial heat decarbonisation is perceived as one of the greatest challenges in the sector. There are numerous promising technologies available such as High Temperature Heat Pumps (HTHP), but there are still barriers to overcome in both costs and Technology Readiness Level (TRL) for their wide implementation, especially for high temperature heat demands above 400 ºC [25]. The list of electrification technologies is still growing, comprehending replacing conventional fossil-fuelled furnaces with electric furnaces, or transforming completely a process, as exemplified by steel decarbonisation via hydrogen-based direct iron reduction [26].

Despite being a non-fossil-based technology, nuclear energy presents disadvantages, including the non-renewability of the fuel, the uneven geographical distribution, as well as the significant CAPEX (Capital Expenditure) required. These factors, coupled with the rapid price decline of renewable power sources such as solar photovoltaic (PV) and onshore wind (Figure 7), position renewable energy as the most compelling technology [27]. Notably, these technologies exhibit lower Levelized Cost of Energy (LCOE) than the cheapest fossil fuel alternative. Nevertheless, new challenges arise that need to be tackled such as grid stability control and alternative market pricing strategies, particularly concerning Variable Renewable Energy (VRE) sources integration [25].

Figure 7. Global weighted average LCOE from newly commissioned, utility-scale renewable power generation technologies, 2010-2022. [27].

Pushed by the expenditure decrease, renewable electricity capacity additions almost doubled worldwide from 2022 to 2023, reaching an estimation of 507 GW installed. Most of the additions were led by solar PV plants. In Europe, the trend is similar, accounting for over 70% of the expansion capacity to solar PV and another 26% to wind technologies [28]. The renewable share increase, however, is increasing concern on new problems such as grid congestion and curtailment. These problems can be mitigated by improving internal energy markets as well as grid reliability and flexibility [29] by favouring demand-shifting and energy storage projects. At very high shares of VRE, electricity systems will require greater flexibility that the one provided by demand-shifting, and the role of energy storage will be crucial to guarantee high cross-sectorial renewable integration shares [30], [31]. In the EU's electricity system, the renewable energy share is estimated to reach around 69% by 2030 and 80% by 2050, from 37% in 2021 [32].

1.4. Energy Storage Technologies

Energy storages enable the independency between energy generation and consumption in contrast with current grid operation, as well as providing resilience to blackouts avoiding costly disruption in normal operations [33]. Energy storage is required for flexibility services ranging from the ultra-short- to the long-term, as well as different response times [34]. These services include maintaining frequency stability by balancing supply-demand imbalances, among others listed below depending on the battery grid location (Figure 8). The possible applications and revenues stream are significantly dependent on the application type, as well as the role of the user in the grid: generator, transmission and distribution, and consumer. In the case of commercial and industrial users, the main application is associated with increased self-consumption of renewable assets, fixed charge and variable charge reduction enabling flexibility and optimising the use of existing assets. Among the ancillary services that could provide power quality, power recovery following outage, and back-up power are highlighted [35], [36].

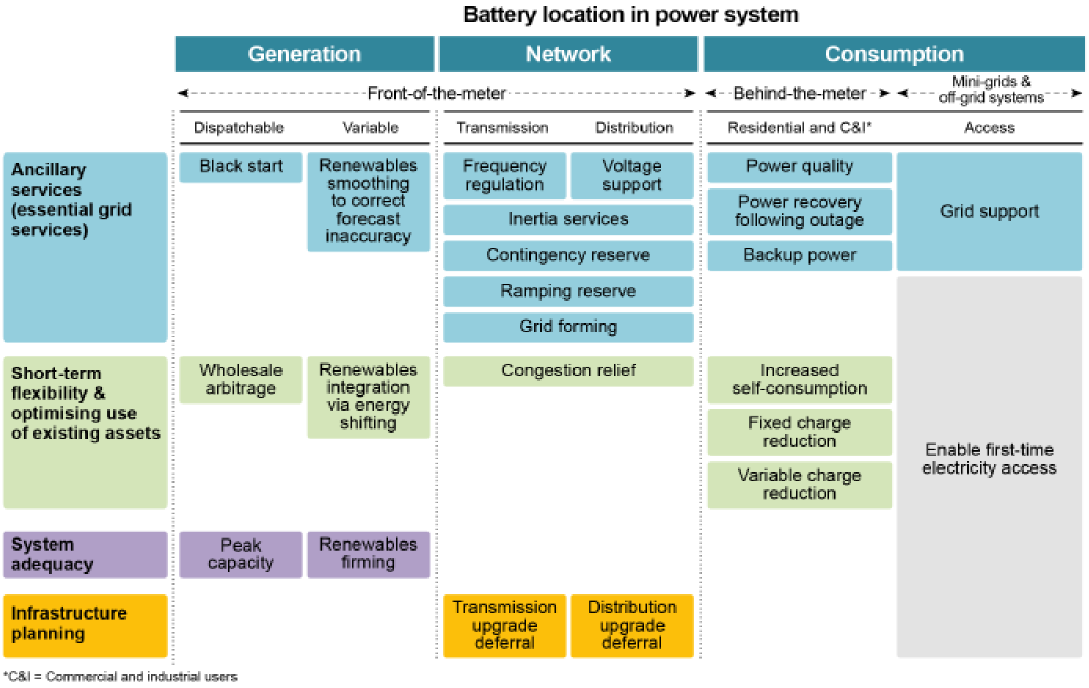
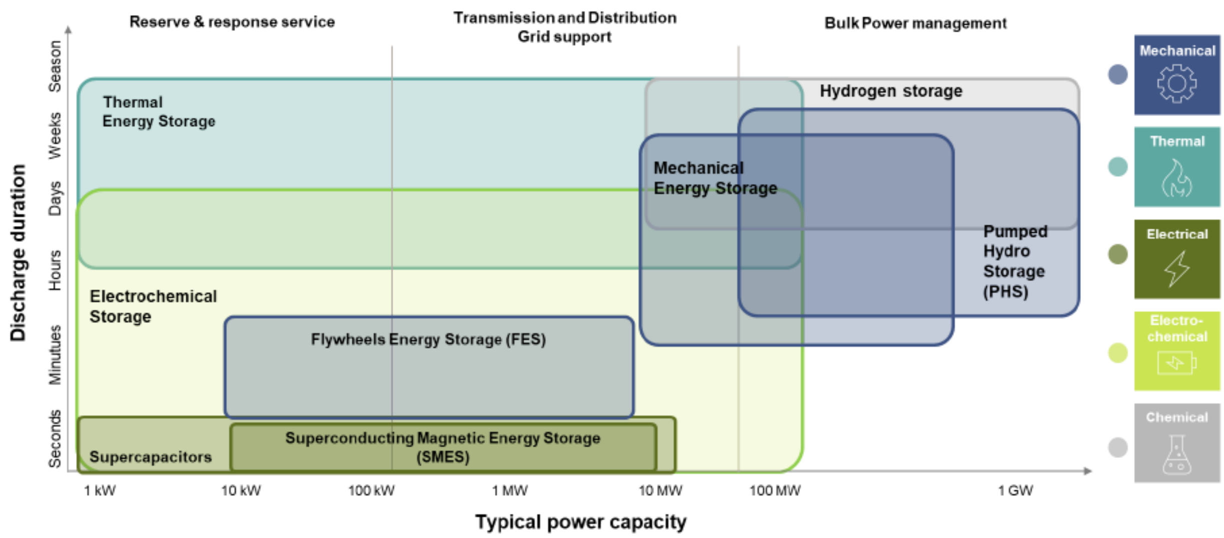


Figure 8. Battery Storage in Power Systems. [36]

Note: Battery storage applications are represented along the dimensions: horizontal axis shows the location within a power system; vertical axis shows the type of services.

Unfortunately, there is not a perfect solution that can provide energy under all these possible circumstances combinations, being this the reason why the list of possible and available technologies is quite long and still increasing. Technologies are usually classified depending on the energy storing mechanism into mechanical, thermal, electrical, electrochemical, and chemical energy storage. Although descriptive, further classifications considering the power capacity and discharging times are more useful to understand the capabilities of these technologies (Figure 9) [31].



Source: Global Data (2019), IRENA (2020), WEC (2020), BNEF (2020), EU (2020), HEATSTORE project (2021)

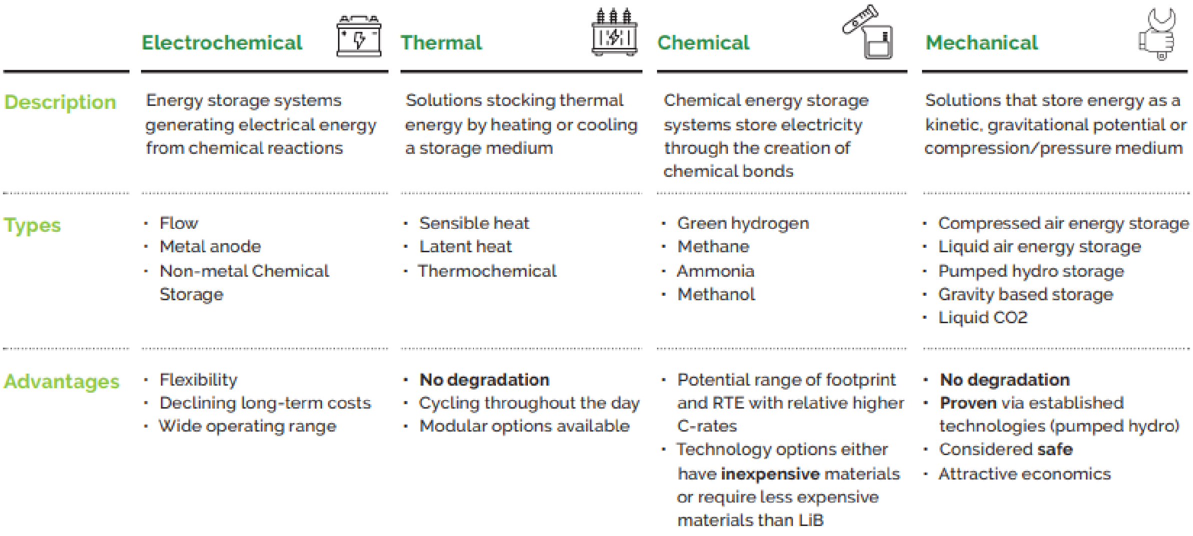
Figure 9. Typical power ranges and discharge duration of different energy storage technologies. [31]

These big families encompass a range of technologies and chemistries. The maturity level, as well as the performance may vary between one another significantly despite being in the same category. Significant researching efforts aim to improve current technologies characteristics, as well as alternatives to diversify the dependence on critical raw materials, being a field of great interest and future prospective [37].

Technology diversification is also a strategy to reduce the dependency on critical raw materials, transitioning from one universal solution to a more personalised market fit for each application. Cost sensibility in the utility sector is higher than in mobility, whereas the performance requirements and volume restrictions show a different pattern. The good understanding of energy demand profiles and requirements are a key factor to consider in decision making analysis incurring energy storage. Electricity, heat and hydrogen sectors are becoming increasingly interconnected, rising the attention of an integrated analysis to assess the cost-optimised mix of flexibility solutions for the heat and power sectors [38].

The focus of this project will be Behind-The-Meter (BTM) industrial applications, regarding the core business of the company assessed Build to Zero [39]. The power capacity in this application is one of the most desired characteristics, as well as intermediate discharge durations ranging from hours to multiple days. This zone is usually referred as Long Duration Energy Storage (LDES) technologies, which can not only address electricity, but also heat needs for thermal energy in some cases. When coupled with renewables, LDES could help reduce 8 billion tons of CO_2 emissions in the industrial sector [40].

The main energy storage categories that fall into this region are electrochemical, thermal, chemical, and mechanical (Figure 10). Whereas the company's currently available product is based on Thermal Energy Storage (TES), previous hydrogen and batteries storage comparisons against the current product have been carried out.



	Electrochemical	Thermal	Chemical	Mechanical
Description	Energy storage systems generating electrical energy from chemical reactions	Solutions stocking thermal energy by heating or cooling a storage medium	Chemical energy storage systems store electricity through the creation of chemical bonds	Solutions that store energy as a kinetic, gravitational potential or compression/pressure medium
Types	· Flow · Metal anode · Non-metal Chemical Storage	· Sensible heat · Latent heat · Thermochemical	· Green hydrogen · Methane · Ammonia · Methanol	· Compressed air energy storage · Liquid air energy storage · Pumped hydro storage · Gravity based storage · Liquid CO2
Advantages	· Flexibility · Declining long-term costs · Wide operating range	· **No degradation** · Cycling throughout the day · Modular options available	· Potential range of footprint and RTE with relative higher C-rates · Technology options either have **inexpensive** materials or require less expensive materials than LiB	· **No degradation** · **Proven** via established technologies (pumped hydro) · Considered **safe** · Attractive economics

Source: LDES Council, Roland Berger

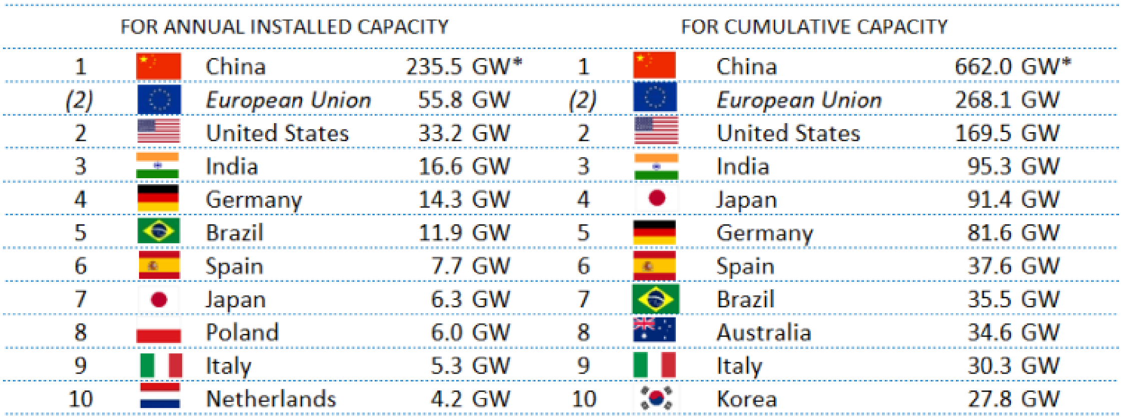
Figure 10. Long Duration Energy Storage categories. [40]

Given the recent development of redox flow batteries as a stationary energy storage, this technology seems to be a promising solution for industrial users. Its main advantages are long lifetime, power and energy decoupling and high efficiency [41], qualities highly appreciated for industrial applications. A further analysis is required to determine which industrial profile better suit this technology and could be a prospective threat or addition to their product offer in the short or medium term.

The economic viability of energy storage devices and batteries deployment is highly dependent on the application and circumstances of the particular case. Among others, the region and the characteristics of the electric system and regulatory environment can heavily shape the boundary conditions [36]. In this project, the region considered for the analysis will be Spain due to the high VRE deployment and low energy prices.

1.5. Spain industrial decarbonisation context.

Spain stands as a forefront in the installation of renewable energy capacity, especially due to the availability of favourable weather conditions. The significant price dropped of this technology in recent years has rendered them more cost-effective than conventional energy sources. Among the weather indicators, the high sun irradiance positions Spain as a good candidate to allocate VRE, particularly in solar technologies, thus attracting private investment in these systems [27], [42]. Spain has been a leader in technologies like Concentrated Solar Power (CSP) plants, accounting for the highest power capacity in Europe [43] and Solar PV, ranking fifth globally and second in the European Union in terms of installed capacity in 2023 (Figure 11) [44].



FOR ANNUAL INSTALLED CAPACITY			FOR CUMULATIVE CAPACITY		
1	China	235.5 GW*	1	China	662.0 GW*
(2)	*European Union*	55.8 GW	*(2)*	*European Union*	268.1 GW
2	United States	33.2 GW	2	United States	169.5 GW
3	India	16.6 GW	3	India	95.3 GW
4	Germany	14.3 GW	4	Japan	91.4 GW
5	Brazil	11.9 GW	5	Germany	81.6 GW
6	Spain	7.7 GW	6	Spain	37.6 GW
7	Japan	6.3 GW	7	Brazil	35.5 GW
8	Poland	6.0 GW	8	Australia	34.6 GW
9	Italy	5.3 GW	9	Italy	30.3 GW
10	Netherlands	4.2 GW	10	Korea	27.8 GW

Figure 11. Top 10 countries for annual (left) and cumulative (right) installed PV capacity in 2023. [44]

As of May 2024, the national grid accounts for 2,304 GW of CSP, 26,261 GW of solar PV, and 30,989 GW of wind technologies [45]. The high capacity has led to higher renewable electricity shares, contributing to a halving of the average final electricity price compared to 2022 levels [46]. Despite electricity prices in 2022 being higher that in the previous decade, Spain's prices were comparatively lower than other European energy markets, a phenomenon known as "The Iberian Exception" [47]. One contributing factor to Spain's comparatively lower prices is the significant share of renewable energy production. This is a great claim for investment and industrial development in the South of Europe, especially sustainable industries.

Beyond these clear advantages, Spain and the Iberian Peninsula are an interesting and peculiar case in terms of electricity markets. The grid interconnections to the rest of Europe are not as robust as other countries, mainly due to geographical complexities [48]. The interconnections between Spain and France are highly congested, which leads to the Iberian electricity market to operate as a separate system in the electricity price biding most of the time [49].

Spain energy context is highly influenced by its strategic geographical situation, close to Africa and America by both the Atlantic Sea and Mediterranean for maritime commerce. A benefit example would be the leader role on regasification stations in the EU, accounting for seven operational terminals, the highest number along with France [50].

Equivalent CO_2 emissions are considered as the measuring unit to encompass the effect of all the GHG emissions in one measurement, being CO_2 selected due to the higher emissions and stability duration in the long-term. The gross emissions profile (Figure 12) excluding those associated with the Land Use, Land Use Change and Forestry (LULUCF), measured in equivalent CO_2, has undergone significant changes throughout the years, mainly driven by the economic and demographic trends. Noteworthy periods include emissions growth from the 1990s and 2008, followed by a steep reduction post-2008 economic crisis until stabilization around 2013. The year 2019 showed a sharp reduction due to the COVID-19 pandemic, but it was followed by an increased associated with the post-pandemic economic recovery. The energy sector and Industrial Processes and Product Use (IPPU) sectors primarily shape this emissions curve [51]. The connection between economic growth, industrialization and emissions should be decoupled in order to achieve the sustainable development goals and one of the main challenges Spain and the world faces.

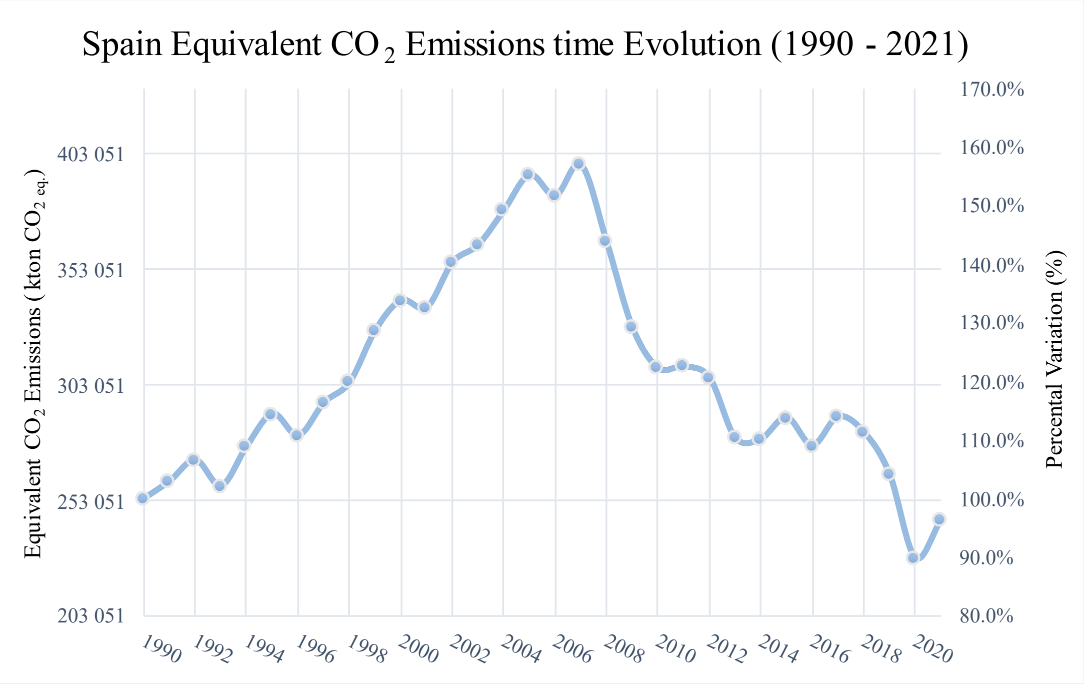


Figure 12. Spain CO₂ emissions time evolution (1990 – 2021). Own calculations based on data available in [51].

The main decarbonisation route is cross-sectorial electrification and decarbonisation of the national energy grid. This trend is aligned with the European strategies, as stated in the Spanish Integrated National Energy and Climate Plan (NECP, *PNIEC* in Spanish). This document is focused on five main dimensions that will be covered in this project: decarbonisation, energy efficiency, security of supply, inner energy market, and research, innovation and economically competitivity. Among others, it is highlighted the consideration to climate change negative effects adaptation and switch from the generation-focused electricity grid to the demand shifting and storage, as well as the higher efforts required in energy storage applications in the industrial sector [52]. Considering this context, the decarbonisation goals listed in the National Plan in Energy for 2030 are as follow:

- 40% reduction in GHG emissions, considering 1990 as the base year.
- 32% renewable energy over the final gross energy end-use.
- 32.5% energy efficiency improvement.
- 15% interconnection improvement with member countries.

Nonetheless, it needs to be considered the importance of hydroelectric as a renewable energy source. In the upcoming years, Southern Europe is expected to reduce its water availability as a consequence of climate change. The IPCC foresees with high confidence a high risk of desertification in the Iberian Peninsula, led by water drought and extreme temperature episodes [5], [53]. Not only mitigation, but also adaptation to climate change needs to be considered in the future model, acknowledging the limitations on both water and other critical raw materials for the energy transition. Techniques that allow to introduce a higher share of VRE needs to be implemented, considering the grid stability constraints [37].

The synergy between the public-private sector is key in this stage of the energy transition, as the technology is ready to implement. An example of strategy to consider is the Strategic Project for Economic Recovery and Transformation (SPERT, *PERTE* in Spanish) fostered by the Spanish Government, under the legislative framework of the Recuperation, Transformation and Resilience Plan. In the list of twelve target topics, one is specifically related to renewable energy, green hydrogen, and storage, and another one to industrial decarbonisation [54]. This is a sign of the importance of both challenges for the Spanish economy. The remaining plans are directly or indirectly related to climate change mitigation and environmental protection.

The installation cost drop combined with the availability of renewable resources make Spain a great country to invest in. The competitive energy price derived from renewable energy makes both the retrofitting of current facilities and new investment appealing for decarbonisation and energy transition projects. All these benefits are prominent for the country to be an early adopter in energy transition technologies, especially those highly affected by the energy price as the industrial sector decarbonisation via electrification. Given this reason, the scope of this project will be based in Spain.

2. Methodology

The focus of this project is the industrial decarbonisation, aligned with the company's mission. As a company where research and innovation are the centre of the core business, the study of both short and long-term is one of the key areas to improve the company resilience and future expansion.

Acknowledging this framework, the aim of this project is assessing the feasibility and potential deployment of redox flow batteries in the industrial sector. The scope of the project focuses on Spain, as justified in the previous chapter for the promising energy landscape. The intermediate sub-questions to answer are as follow:

- Evaluate current and future energy, decarbonisation and industrial scenarios in Europe and Spain.
- Recognition on current energy storage alternatives, focusing on flow batteries.
- Techno-economic assessment of flow batteries as decarbonisation technology in the industrial sector.
- Identify challenges and prospective scenarios where it would be of value or risk for the company market niche, where capacity is highly valued.

In order to do so, the following methodology has been proposed (Figure 13).

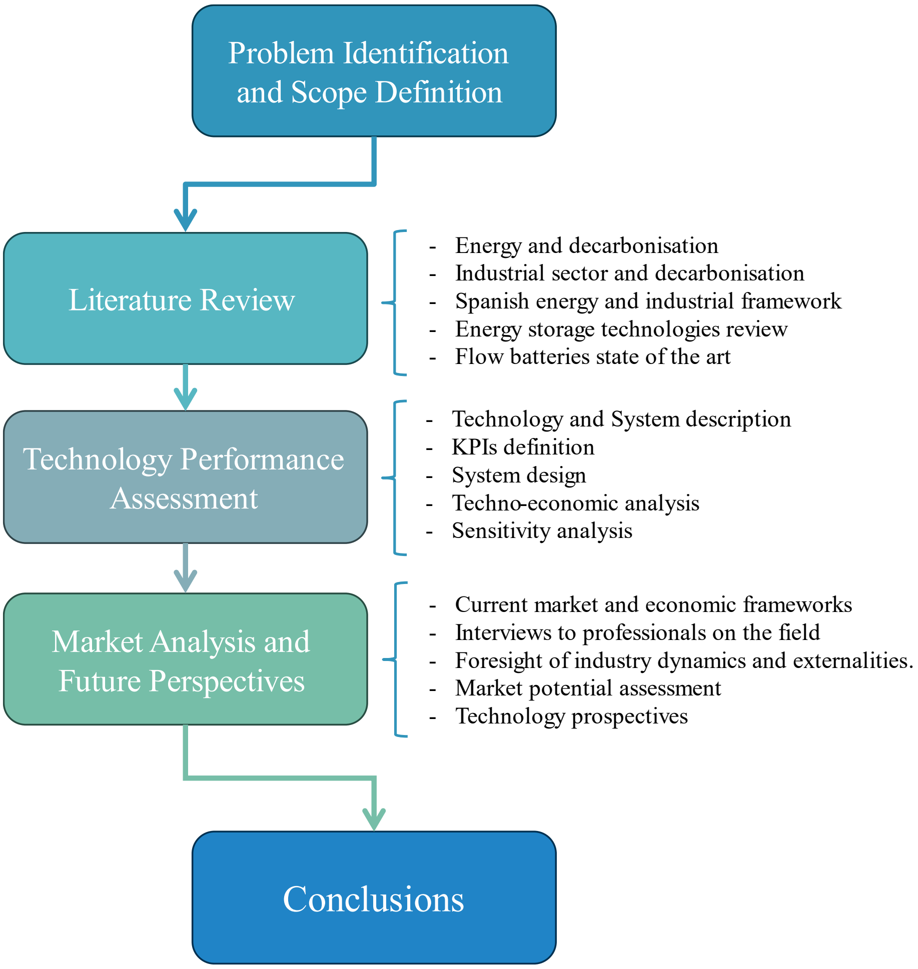


Figure 13. Project methodology scheme.

The initial step involves identifying the problem and defining its scope. Once the studying scope has been established, a literature review is conducted. Key areas of focus include the energy and decarbonisation framework, the characterisation of the industrial sector, and the specific decarbonisation needs within the Spanish energy and industrial context. On the technological front, a review of current energy storage technologies is conducted in order to provide background information on the sector. Finally, the state of the art in redox flow batteries is examined to determine the most promising technology for the defined scope.

Once the technology is identified, a performance and system analysis will be conducted to evaluate its suitability for providing the required service in a representative industrial case within the company's market segment. This process will enable the Key Performance Indicators (KPIs) identification for both the battery system and the application, allowing for better tracking of their evolution over time. The framework for this definition will follow a *Mutually Exclusive and Collectively Exhaustive* (MECE) analysis.

After identifying the main KPIs and considering the battery operations and limitations, the system design and sizing will be conducted. This step serves as the preliminary phase for the techno-economic analysis, which aims to understand the factors most affecting the technology's cost-effectiveness. The results will enable a cost comparison of different technologies using standard metrics, facilitating extrapolation to other technologies if needed in future analysis. Additionally, a sensitivity analysis will be performed to assess the impact of the most critical parameters.

Upon obtaining the results, their relevance will be discussed, and the market potential assessment will be conducted using the *Futures Thinking* methodology. This approach is based on current market and economic frameworks, identifying signals of change and insights to explore alternative futures. It enhances industry foresight, improving the decision-making process [55]. In order to gain a deeper understanding of sector dynamics, interviews with industry professionals in the field have been conducted. The gathered information and results will be used to project industry incentives and barriers that could either support or hinder the development of redox flow batteries. A market potential assessment within the project scope will then be conducted, and the technology's prospects will be identified for further consideration.

2.1. Software selection

Battery modelling remains a research and development challenge for research, particularly for non-lithium-based batteries [37]. The need for digital twins and energy management tools that assist industrial operators in a user-friendly manner is a pending task for energy engineers and digitalisation. The selection of software has considered the user-friendly interface and data visualisation capabilities, as well as the computational flexibility to model different system and optimisation algorithms. Notably, the ability to handle diverse data and perform different optimisation methods is highly valued due to the significant number of variables expected. As an example, hourly electricity price is one of the key parameters to consider, along with the diverse industrial energy profiles that may vary from day to day.

As regards the techno-economic analysis, Microsoft Excel has been the software selected due to the license availability and capabilities that fall under the scope defined. Most data required is often adapted to Excel format, due to its widespread use, being the reason of selection for the purpose of the project. Further implementation and study of the technology should consider higher performance and level of detail for the characterisation of the technology and coupling if the results of the techno-economic and market assessment are positive towards the new technology.

Given its versality in integrating and comparing different technologies, performing optimisation algorithms, and managing vast and diverse datasets, one of the software considered is MATLAB Simulink. This analysis could be beneficial at a design phase, rather than a techno-economic analysis being the reason why it has been discarded for now.

Table 1. Software comparison summary.

	COMSOL	**MATLAB**	**Excel**	**Open Modellica**	**TRNSYS**
CFD capability	Yes	It can be coupled with COMSOL LiveLink	It can be coupled with COMSOL LiveLink	Yes	Yes
Coupling capabilities	Yes	Yes	Yes	No	No
License	€€€	€€	€	Open Source	€€
User-friendly	Medium	Medium	High	Low	Medium
Optimisation	Device level, limited range of algorithms	System level, wide range of algorithms	System level, limited range of algorithms	Device level, wide range of algorithms	System level, medium range of algorithms

Among the main improvements, the use of COMSOL software via Livelink connection has been explored, in order to better characterise the redox flow battery under consideration using Computational Fluid Dynamics (CFD). Livelink enables connection to both Microsoft Excel and MATLAB. A model has been developed to understand the battery physics and dynamics, as well as the possible challenges during its modelling for future research.

Regarding alternatives for CFD, TRNSYS and Open Modellica use was considered. Open Modellica was advantageous as it is an open source widely used in the European research landscape [56]. However, the data visualization and lack of available developed models of the technology understudy ranked this option as the least favourable one. Another multi-physic discrete system software considered was TRNSYS, which has a wide user-base, including optimization, energy system research and emerging technology assessment [57]. However, as disadvantages when compared to the other alternatives, it is neither an open source nor a flexible tool to compare and manage data as Excel or MATLAB is. Thanks to LiveLink, this disadvantage can be omitted by linking the system integration to COMSOL results [58]. COMSOL has a guide on model development for vanadium redox flow batteries [59]. Once this type of redox flow was chosen, the convenience of comparing the already existing model emphasized this powerful combination.

2.2. Target Client Segment Identification

As mentioned earlier, one of the main steps in developing a new product in the market is the identification of the target client segment. Methodologies as *Design Thinking* are based on the development of products based on the clients' necessities instead of the technological focus that represented the previous design methodologies. The implementation of this methodology is key in the launch and analysis of products threat as the final decision in the market will be taken by the clients. For this reason, specifying the hypothesis of the pains and gains, as well as their jobs and relieves are a good strategy to estimate the possible decisions the client will make.

Current company's target customer segment are industrial facilities that demands industrial process heat, considered as BTM applications. The heat demand temperature is below 400ºC, and the power can oscillate between 1 MW and 5 MW. Within this power range, the user interacts with the grid mostly by optimising energy contracts namely Power Purchase Agreements (PPAs), self-generation or modifying the demand. Demand-shifting is associated to energy storage devices rather than energy profile changes considering the clients' characterisation. The energy storing capacity is estimated in 14 hours to harmonize the results, but further optimisation could be carried out based on electricity contracts and renewable energy generation available at the location, for example.

The customer segment main role is to produce goods at the required quality level and lowest environmental impact possible. Their objective is to maximise the benefits that can come from lowering bills, as well as developing a higher value product. In order to do so, a strategy is to reduce the electricity costs by implementing energy storage that enables to meet the production rate requirements. Moreover, a decarbonization of the product energy demand is achieved by properly coupling renewable energy with the industrial demand and storage. This implementation reduces risks of security of supply and exposition to price volatility. Considering the characteristics exposed, the comparison needs to consider the level of service quality and security of energy supply. Considering the results from the review process to the market segment prospective clients and experts on the field, the final parameter for comparison will be the initial investment required and the levelized cost of storage as measures of the economic viability of the propositions. Further comparisons to consider are the energy efficiency, footprint due to the relation with the capital expenditure and viability of retrofitting existing installations, environmental footprint and materials abundance.

2.3. Hypothesis

The measured time step in the industrial energy demand data set available is 15 minutes, value that can be used in the system modelling. This time step is large enough to cover the transient effects on the model and simplify the model if required for further Battery Manage System (BMS) and Energy Management System (EMS) development.

Considering the availability of data in literature, it has been estimated that the stacks are coupled between them resulting in a larger stack. By these means, validated data can be employed in further model development considering the viability of the product in this initial project. However, experimental results carried out by the interested party are recommended in order to diminish the deviations between the equipment and the expected outcomes.

The operation of the cell has been estimated as one cycle per day in the levelized cost of storage as reference. This hypothesis seems reasonable considering a high VRE grid, especially solar PV as it is the case of the scope considered. More precise operation and optimisation techniques need to be implemented in order to better couple the indicator with the case, especially if especial tariffs or PPAs are conducted. This approach does not affect the comparison of technologies under the same parameters, giving a general idea of the effect that different electricity prices and schemes can impact on the products compared. Nonetheless, it could be beneficial to adapt the model parameters to the case in order to obtain a more precise value.

Losses effect has been grouped in the techno-economic analysis and attributed to the charging electricity required. This hypothesis is valid for locations where temperatures oscillate within 10-40ºC, as the thermal energy demand does not impact significantly. For other thermal requirements, a further analysis and estimation of the thermal energy demand needs to be conducted as it could significantly affect the viability of the product.

3. Energy Storage State of the Art

Energy storage has played a major role in humanity evolution and adaptation to climate since the initial wood storing for heating purposes to more complex and revolutionary systems such as lithium-ion batteries. However, energy storage role in the energy transition is rising importance, especially for VRE storage, requiring new and more sophisticated energy storage systems [33].

Hydroelectric generators are considered the only renewable energy that can be controlled. Unlike sun and wind-based technologies, the production of electricity can be adapted according to the demand. A factor that needs to be considered in energy planning is the expected hydroelectricity availability. In many regions, such as the Iberian Peninsula, there are already restrictions in water consumption [60], limiting the reliance on this renewable source. This negative effect of climate change highlights the need of implementation of alternative high variable renewable energy technologies at a faster pace in order to achieve climate neutrality goals [53]. Intrinsically, a major problem arises concerning the grid operation and voltage and frequency stability when increasing the variable electricity production share.

Conventionally, electricity production was coupled with the demand, which dictated the electricity production profile. The importance of demand-shifting strategies is arising as the VRE implementation increases. The simplest solution is to adapt the demand to the renewable production, but the most inconvenient one for energy end-users. Aiming to diminish the impact on end-users' comfort, the arising of energy storage to achieve the renewable energy share goals is required [61].

One of the main challenges of this broad technology group is that there is not a "fit for all" solution. This is the case of most climate change mitigation and adaptation measures, where the context and resources availability play a major part on the solution implementation viability, attractiveness and effectiveness. The consumer and generator highly determine the best energy storage solution to couple with. Among the main parameters, the cost, storing time, lifespan and life cycle, energy and power gravimetric and volumetric density are highlighted [62]. The relative importance of these factors can decide which technology is better suited for a specific application and electricity profile.

Energy storage technologies are usually divided into families considering the storing energy mechanism: mechanical, electrical, thermal, and electrochemical storage (Figure 14). Among the technologies considered, Pumped Hydropower Energy Storage (PHES) is the most mature and abundant for grid connected storage [63]. However, its deployment is highly linked to geographical availability and the global capacity is close to reaching the maximum installed capacity. Another mechanical large-scale storage system is Compressed Air Energy Storage (CAES), which can reach high energy capacity values. However, the main disadvantage is the low efficiency below 70% or even 45% [64]. Lastly, on the lower capacity and discharge time zone, flywheels are highlighted for stationary mechanical storage [63].

Electrical storage is often associated with high power density devices such as Superconducting Magnetic Energy Storage (SMES) and supercapacitors, like the Electric Double Layer Capacitor (EDLC). However, the low energy density leads them to short storing periods based on the self-discharge phenomenon [64].

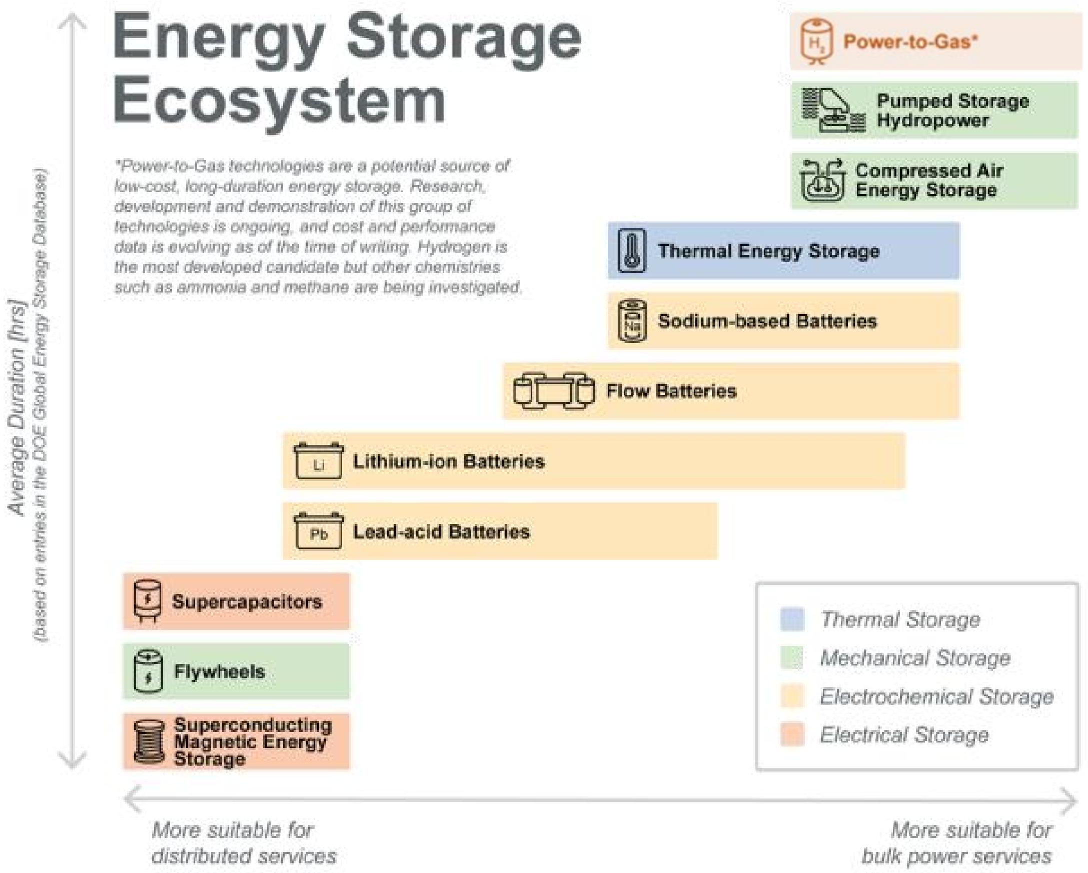


Figure 14. Ecosystem of energy storage technologies and services. [63]

In BTM applications, electrochemical, thermal and chemical storage are the dominant technologies. Under the chemical energy storage category, power-to-gas, large-scale hydrogen storage, thermochemical energy storage and traditional energy storage of natural gas, oil and coal are highlighted [33]. However, in the latest years power-to-gas and hydrogen storage for power-to-power applications is often associated with electrochemical storage due to the prominence of green hydrogen production via water electrolysis and fuel cells deployment [64], [65]. Moreover, thermochemical energy storage is connected to thermal energy storage as the transformation processes involve heat transfer mechanisms [25]. Other relevant emerging chemical energy storage technologies are ammonia, methanol and synthetic fuels.

The focus of this project is Long Duration Energy Storage (LDES) technologies, which are defined as the gap between short-duration and seasonal energy storage technologies. The dividing line between LDES and short duration is not so well-defined, and it can vary from one reference to another. However, there is a consensus in the definition that states that the limit is on the maximum discharging time at which lithium-ion batteries stop being the most cost-effective option (Figure 15). This value can oscillate between 4 and 10-hours discharging duration, which is related to the energy capacity and the current cost of lithium-ion batteries [61], [66], [67].

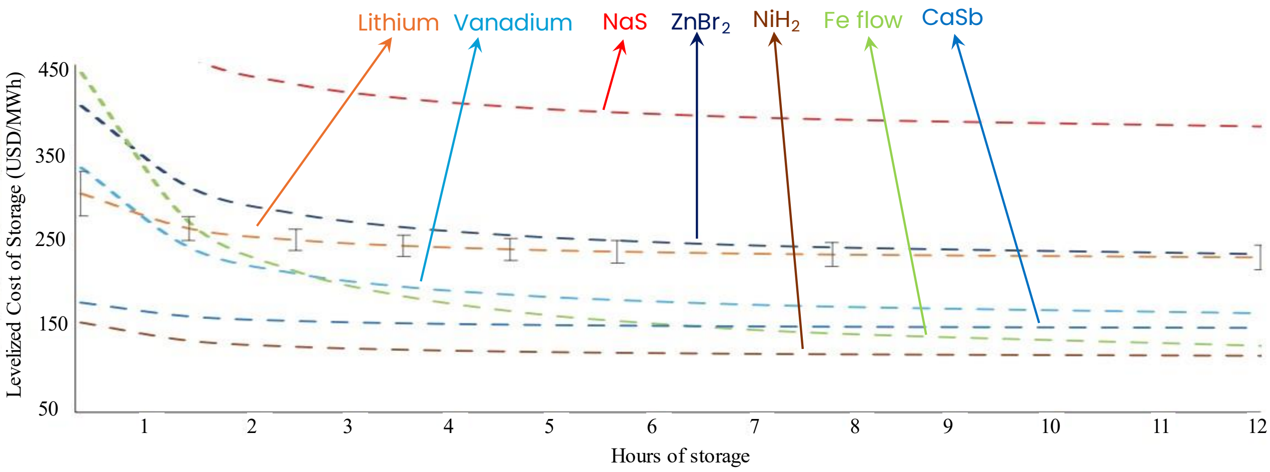


Figure 15. Levelized cost of storage of battery technologies operating at 600 cycles per year. [67]

Thermal and some electrochemical storage fall under the LDES region, focus of this project, being the reason why more detailed study will be conducted.

3.1. Thermal energy storage

Thermal Energy Storage (TES) enables to decouple heating and/or cooling demand from power generation, leading to greater efficiency, flexibility, security, and reliability in energy supply in these applications due to the wide temperature operating range in storage mediums [68]. TES technologies are commonly divided into three main typologies namely sensible, latent and thermochemical energy storage. Both the operating temperature and storing time ranges differ from one technology to another (Figure 16).

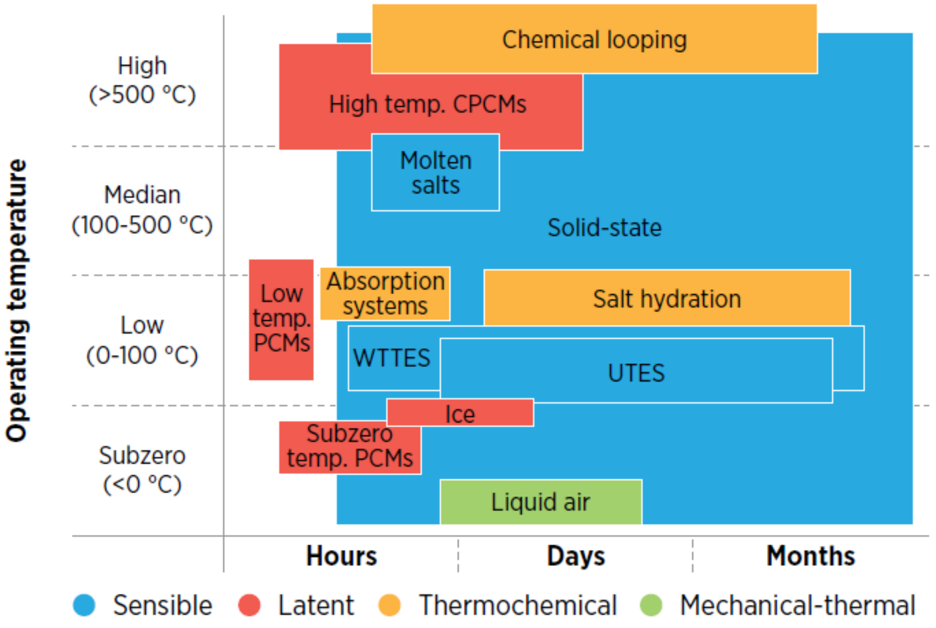


Figure 16. Operating temperatures (vertical axis) and storing energy time ranges (horizontal axis) for TES technologies. [68]

3.1.1. Sensible heat energy storage

Sensible heat energy storage is based on the temperature change of materials as storing mechanism [69]. An example would be a Water Tank Thermal Energy Storage (WTTES) which can be used from domestic to industrial end-users, commonly used for temperatures below the 100ºC due to the vaporisation point at ambient pressure [70]. For instance, another relevant and conventional technology type under this category is Underground Thermal Energy Storage (UTES). Further examples of heat transfer and storing materials are molten salts, commonly used in CSP power plants due to the higher temperature allowance, being of greater relevance for industry. Finally, solid-state energy storage, including different materials such as ceramics, sand, and concrete [69]. This category is still under the demonstration phase but shows a greater operational temperature potential, expecting to surpass 700ºC by 2030 [68].

Sensible heat is by far the most commercially successful technology on residential and industrial scales, ranging from hourly to weekly storage duration use cases [38], [69]. The market counts with a high number of technology providers, being the high efficiency reached one of the main triggers of its success [25].

3.1.2. Latent heat energy storage

Latent heat takes advantage of the higher specific energy density when materials are changing its phase. The energy density highly increases, reducing the footprint of the technology. Additionally, as phase change is an isothermal process, the more stable discharge temperature supposes a performance improvement when compared to sensible heat. On the other hand, expense and volume change are the main disadvantages, being preferably the solid-liquid process rather than gas involving techniques [69]. Among others, this technology can be divided into sub-zero, low, and high temperature Phase Change Materials (PCM). Ice is highlighted as it has been the most ancient latent thermal storage used for centuries. However, in this project the focus will be heating demand rather than cold chains given the dominant heat share in the energy used. PCM materials development is one open area of research.

Despite some demonstration plants have been developed for high temperature PCM in industrial applications, still some challenges need to be overcame in order to incentivise commercialization. Cost, material and operational improvements remain an issue to overcome in the next five years [68].

3.1.3. Thermochemical energy storage

Finally, thermochemical energy storage is based on endothermic and exothermic reactions. They can operate in two ways, namely chemical reactions and sorption processes [33]. In chemical reactions energy is stored in chemical bonds and heat is exchanged with the storing medium as heat fluxes of the reversible reaction. In sorption processes, thermal energy is stored either through physical bonding, named adsorption processes, or dissolution of a material, named absorption [69].

Absorption systems and chemical looping are highlighted typologies. Depending on the chemical reaction, a heat flux is conveyed either to the storing medium or heat transfer fluid in contact. Thermochemical energy storage can significantly improve the TES footprint given the high energy density [68], being able to store energy from hourly to monthly durations [38]. Nonetheless, it is a relative nascent technology, with a TRL ranging from 4-6 [69] requiring further research in order to bring the technology to market [25].

TES can enable cost-efficient electrification of most heat applications, commonly referred to as Electrothermal Energy Storage (ETES). Although there is some room for improvement on the technology performance, there are already mature commercially available technologies, notably on sensible heat. ETES can provide in some cases a more competitive industrial heat decarbonisation, by increasing the system efficiency up to 90-95%, as well as reducing investment costs when compared to electrochemical batteries [25]. Application oriented decision criteria should be carried out when designing and coupling both the energy storage techniques and energy management system. In this project, sensible heat energy storage is compared as a benchmark of the company current product to redox flow batteries.

3.2. Electrochemical Storage

Electrochemical energy storage interconverts chemical and electrical energy through reduction and oxidation reactions, commonly referred to as redox reactions [71]. This type of reaction involves the transfer of electrons from one chemical species to another. Direct redox reactions lead to the oxidation and reduction of the species in the same vessel, converting chemical energy into heat. This is the case for combustion where a fuel is oxidised in contact with an oxidant agent [72]. In indirect reactions, oxidation (anode) and reduction (cathode) reactions are divided into two separate halves, leading to an electron flow between the electrodes. This electricity can be used when coupled to an external circuit or load, often modelled by an external resistor (Figure 17). The latter ones are the ones commonly used in batteries, either primary or secondary. Given the requirement of long life, the scope of the project will consider secondary batteries, also named rechargeable batteries [72].

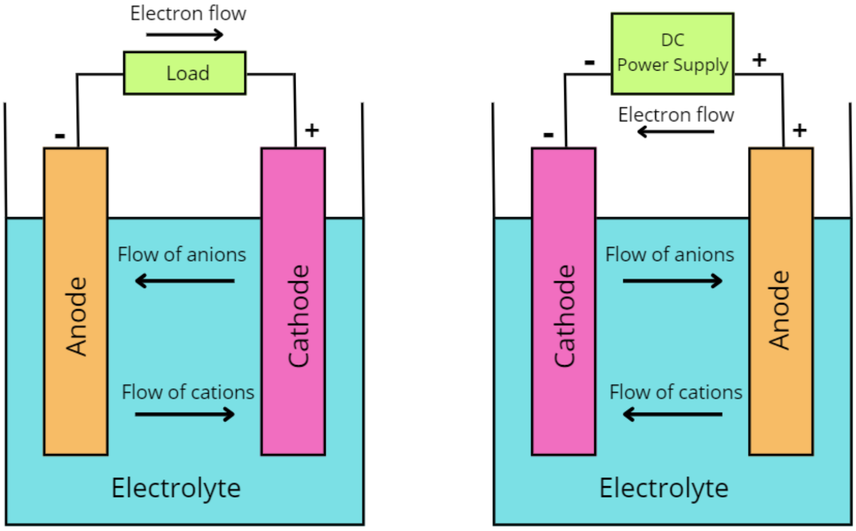


Figure 17. Electrochemical operation of a cell schematic (Left: discharge; Right: charge). Redrawn from [72]

The most popular secondary batteries at present are lithium-ion batteries (LIBs) given the significant development in recent years, significantly improving the technology performance. The fast development linked with the uptake of economies of scale had led to a drop in cost from an average battery pack price of 780 USD/kWh in 2013 to 139 USD/kWh in 2023, referred to 2023 US dollars [73]. Far from stopping, this trend is expected to continue in the immediate future, fostering the capacity increase along all economic sectors [74].

As previously discussed, the higher energy density makes LIBs the prevailing technology in mobility applications, with Electric Vehicles (EVs) accounting for over 90% of the LIBs demand increase from 2015 to 2023 [36]. Most stationary applications are still cost-sensitive for LIBs deployment, requiring even further cost reduction strategies [62]. Post-lithium-ion batteries such as sodium-ion seem like an interesting option for this sector as cost is reduced as well as critical raw materials dependence. Despite the cost reduction, LIBs are not cost-effective for stationary applications that require discharging times higher than 6 hours, benchmark for LDES [36].

Given the long list of electrochemical batteries chemistries and configurations, the performance heavily differs from one technology to another. In Table 2, a comparison between the main technologies discussed, including LIBs, Super Capacitors (SC), Sodium-Sulphur (NaS), lead-acid (PbA) and redox flow batteries (RFB), is presented considering both the battery performance as a system and the application oriented KPIs to consider [75]. Note that despite super capacitors not being an electrochemical energy storage technology the high-power density and fast time response makes it a good choice to couple with electrochemical technologies, being this the motivation of considering it in the comparison analysis among electrochemical batteries.

Table 2. Evaluation of battery and application oriented KPIs for electrochemical storage technologies. [75]

		LIB	**SC**	**NaS**	**PbA**	**RFB**
Battery oriented	Energy density in Wh/kg	●	○	●	◑	◑
	Power density in W/kg	◑	●	○	○	○
	Efficiency in %	●	●	◑	○	○
	Self-discharge in %/day	◑	○	○	●	●
	Reaction Time in s	◑	●	○	●	○
Application oriented	Cost in EUR/kW	○	●	○	●	◑
	Cost in EUR/kWh	○	○	◑	●	◑
	Lifetime in cycles	◑	●	○	○	●
	Shelf life in years	◑	●	◑	○	◑
	Design Flexibility	○	◑	○	○	●
	Ecologic impact	○	●	◑	○	●
	Safety	○	●	◑	◑	●
	Storage duration	min-days	ms-hour	min-days	min-days	weeks

Legend: ○ = negative characteristics; ◑ = medium characteristics; ● = positive characteristics.

Electrochemical systems can be divided into two main categories, namely open and closed cells. In open cells, the energy and power will be provided as long as there is a feed of reactants to the system. However, overall round-trip efficiency is low in these systems. On the other hand, closed systems contain the reactants and the product inside the system, limiting charge and discharge. The power capacity in these systems is strongly restricted, leading to an oversizing strategy that may not be economically viable nor resource efficient. An example of the former is fuel cells where power is provided as long as hydrogen or other fuel is supplied. For instance, the latter category encompasses technologies such as lithium-ion and lead-acid batteries.

An intermediate category has arisen in the last years as a compromise solution between efficiency and power capacity. There are two main examples of these hybrid concepts, where metal-air batteries and redox flow batteries are highlighted [76]. As for the industrial sector, long cycle lifetime is one of the main pains for industrial users, discarding metal-air batteries given the current expected lifetime [61]. On the other hand, RFB seem to be a better option as they show a better capacity and lifespan performance, falling into the LDES region of interest for discharging times over 6 hours. The most mature RFB such as all-vanadium and iron redox flow batteries can even surpass 20 000 cycles in their lifetime, the highest value for electrochemical batteries, which theoretical value is usually below 12 000 cycles [67].

Nonetheless, the main advantage of this device is the partial decoupling between energy and power [41]. Whereas in batteries these values are determined by the reactants inside the device, in flow batteries energy capacity is determined by the vessels size. Regarding power sizing, power is connected to the electrochemical stack design and can be modified by changing the size and number of cells. The number of cells in series determines the voltage, whereas the cell cross sectional area defines the stack current [77]. This decoupling allows to a more tailored power and energy sizing, increasing the cost-competitiveness and footprint of redox flow batteries when compared to lithium-ion and lead-acid batteries [61], especially in use cases where energy and power rating profiles discrepancies are pronounced.

3.3. Flow Batteries State of the Art

Flow batteries are rechargeable batteries that consist of two different electrolytes as storage medium, designated as anolyte and catholyte for negative and positive charge, respectively (Figure 18). The electroactive species are dissolved in electrolyte solutions stored in external tanks that are flown in the stack [76]. Unlike the state-of-the-art LIBs, electrodes function as catalytic sites to electrochemical reactions rather than storing ions, reducing the electrodes mechanical stress.

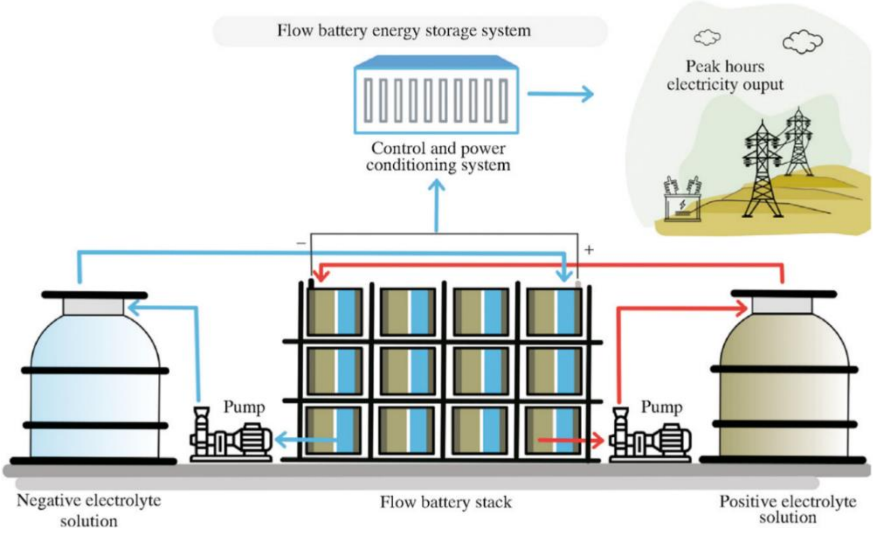


Figure 18. Schematic diagram of redox flow battery energy storage system. [78]

Nonetheless, the first and most important advantage is the decoupling of energy and power density. Additionally, the elimination of ion insertion potentially leads to longer cycle life in RFB. Besides, flowing electrolytes dissipate the limited heat generated by the electrochemical reactions, allowing higher charge and discharge rates without significantly impacting the thermal management consumption or the device safety window [79].

The general advantages across chemistries of redox flow batteries when compared to other energy storage technologies are [67], [76] :

- Good energy efficiency: 60-85%.
- Long cycle lifetime: more than 20 years, especially for all-vanadium technologies.
- Recyclable and reusable electrolyte. Vanadium redox flow batteries account with unlimited lifetime by onsite reprocessing.
- High cycle stability, accounting for more than 10 000 cycles.
- Fast response time ranging from micro- to milliseconds.
- Scalable and modular design, independent for power and capacity.

- Greater overcharge and deep discharge tolerance than conventional electrochemical batteries.
- Low maintenance.
- Almost no self-discharge in selected redox couples.

On the other hand, the main disadvantages for the technology roll-out are low energy densities and high investment costs [76]. Characteristics such as energy and power density, charging and discharging times, lifetime and temperature range heavily vary from one component to another. Therefore, depending on the use case and location the optimum selection of redox pair might differ.

Given the long and diverse list of possible flow battery systems in terms of electrolyte selection, a further analysis on current systems state of the art will be undertaken to better assess the system to model.

3.3.1. Materials

Theoretically, any redox pair could be used for the anolyte and catholyte solutions. However, depending on the parameter that should be enhanced, the best alternative can vary. The electrolyte is identified as the most critical component in RFBs. Commonly, the main parameters to take into consideration when choosing a redox couple are redox potential, solubility, chemical reactivity and stability, cost-effective, safe and abundant active materials [76], [80].

In Figure 19, a summary of possible metal redox couples is represented and ordered by the standard potential. The water stability window for the standard conditions has been highlighted as a reference. Note that the hydrogen evolution reaction (H^+/H_2) takes as potential reference the overpotential associated to carbon electrodes in contrast to the other pairs. Otherwise, its value would be zero as it is considered the redox couple potential reference in standard conditions. Although the number of possible redox couples seems quite extend, the combination of two redox couples with useful voltage and solubility is greatly limited [79].

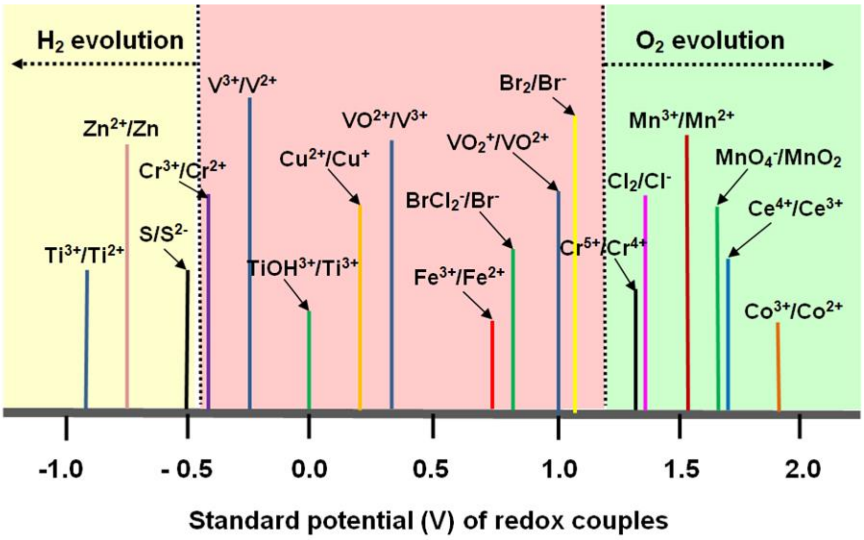


Figure 19. Standard potentials of known metal redox couples in an aqueous system. [79]

In terms of safety and cost, aqueous-based electrolytes are easier to manufacture. Nonetheless, the Electrochemical Stability Window (ESW) is bounded by hydrogen and oxygen evolution reactions to 1.23 V, leading to lower theoretical cell overpotentials and, consequently, lower energy density and higher footprint. However, higher Open Circuit Voltages (OCVs) are possible via kinetic stabilization due to appropriate selection of electrolyte composition and electrode materials [79], [80].

Nowadays, most RFBs use aqueous chemistries. Although this compromise between safety and operational simplicity with energy density could be acceptable for stationary industrial applications, non-aqueous RFBs have emerged as a lever of wider ESW of organic solvents. This change could enable chemistries presenting OCVs higher than 3V, which positively impacts the cost-competitivity of RFB by reducing both energy and power costs [80].

Note that hydrogen concentration variations can modify the absolute ESW potential, while the relative potential is maintained. If the RFB couple considered varies the pH, the OCV will vary with the State of Charge (SOC). In other words, depending on the charging and discharging reactions evolution, the water ESW could shift, leading to hydrogen and oxygen splitting. SOC estimation and safety measures regarding the gassing effect should be taken into account in order to avoid undesired effects.

3.3.2. Families

More than 50 different systems have been described in literature, of which only a small number have been commercialised or are in the commercialisation phase [76]. Redox flow batteries families are usually divided into two categories namely pure or conventional redox flow batteries and hybrid redox flow batteries. All-vanadium redox flow batteries are the most common pure RFB, whereas Zinc-bromine is highlighted in the latter. Whereas the pure RFB are composed by two flowing electrolytes, hybrid RFBs are conformed by at least one solid active material [77].

- **All-vanadium flow batteries**

All-vanadium flow batteries (VRFB) were invented and developed in the 1980s as a promising solution to tackle cross-contamination in redox flow batteries [79]. Unanimously, literature and experts consulted conclude that all-vanadium redox flow battery is the most successful and mature technology so far in redox flow batteries. One of the main reasons is the longer cycle life due to the capability of vanadium to exist in solution in four different oxidation states: vanadium (II) and vanadium (III), both in the positive electrolyte, and vanadium (IV) and vanadium (V) in the negative electrolyte [77]. The involved semi-reactions are as shown:

Cathode:	$\mathrm{VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O}$	$\mathrm{E_{ca}^{\theta} = 1.00\ V\ vs.\ SHE}$
Anode:	$\mathrm{V^{2+} \rightleftharpoons V^{3+} + e^-}$	$\mathrm{E_{an}^{\theta} = -0.26\ V\ vs.\ SHE}$
Overall reaction:	$\mathrm{VO_2^+ + V^{2+} + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O}$	$\mathrm{E_{cell}^{\theta} = 1.26\ V\ vs.\ SHE}$

Note that the reactions have been expressed as direct for the discharging reaction and as reverse direction for the charge. The OCV for each reaction is associated with the Nernst Potential (Eq. 1) under standard conditions.

$$E(T, p_i) = \frac{-\Delta\bar{g}_{reaction}(T, p_o)}{z_F \cdot F} - \frac{R\,T}{z_F \cdot F} \cdot \ln\left(\frac{\prod_R (a_R)^{\nu_R}}{\prod_P (a_P)^{\nu_P}}\right) \qquad \text{(Eq. 1)}$$

Being $\Delta\bar{g}_{reaction}$ the reaction molar variation of Free Gibbs energy under standard conditions, which are associated with the activity of each reactant and products equal to the unit. F corresponds to the Faraday's constant that equals 96 485 C/mol, and z_F the number of electrons transferred in the reaction, which equals one in this case as it can be deducted on the electrodes' reaction. The second term is the one that quantify the effect of the activity of each species, parameter that is linked to the concentration of species. Note that in standard conditions this second term equals zero, being the resulting expression equal to the first term as defined.

The State of Charge is defined as the ratio between the concentration of vanadium (V) in the cathode (Eq. 2a) or vanadium (II) in the anode (Eq. 2b) compared to the overall vanadium concentration in each electrode. If the cells are balanced, then the SOC measured in each cell is the same, as expressed in Eq. 2c [81].

$$SOC_{cathode} = \frac{c_{V(V)}}{c_{V(IV)} + c_{V(V)}} \qquad \text{(Eq. 2a)}$$

$$SOC_{anode} = \frac{c_{V(II)}}{c_{V(II)} + c_{V(III)}} \qquad \text{(Eq. 2b)}$$

$$SOC_{balanced} = \frac{c_{V(II)}}{c_{V(II)} + c_{V(III)}} = \frac{c_{V(V)}}{c_{V(IV)} + c_{V(V)}} \qquad \text{(Eq. 2c)}$$

The standard cell OCV at 25 ºC is 1.26 V, but due to side effects, mainly the Donan potential appearing at the membrane surfaces, the OCV varies with the SOC. Consequently, the OCV ranges from 1.1 V to 1.6 V which depends on the electrolyte solution concentrations [77]. Most commonly, the cell voltage considered is 1.4 V, leading to power and energy densities around 800 W/m^2 and 25 Wh/L, respectively [82].

Vanadium ions are dissolved in a sulfuric acidic solution that can include other additives that inhibit precipitation, among other undesired effects. By enlisting the same element in both positive and negative electrolytes, cross-contamination is reduced and can be electrochemical reversible by charge steps. Nonetheless, the technology is limited by vanadium ion solubility and stability in electrolyte solutions, limiting the energy density to approximately 25 - 35 Wh/L, ten times lower than LIBs. These values are achieved for typicaly commercial vanadium ions concentrations ranging 1.6 – 1.7 M and 2 M sulphuric acid concentrations [77]. The temperature ranges usually oscillate between 10 - 40ºC, but the temperature window could be increased by alterations in the solution composition and additives use that reduce the precipitation risk, enlarging the temperature use range from -5 to 50ºC [79], [81].

The electrochemical system roundtrip efficiency, defined as the ratio between total discharged and charged energy, is quite high as most electrochemical systems. On the other hand, the overall system energy efficiency oscillates between 70 – 85%, mainly due to the auxiliary losses. This consumption is usually linked to the pumps, being the highest parasite energy demand. If ambient temperatures are extreme, the thermal management system may also require an elevated energy demand reducing the overall system efficiency if recurrently the temperature range is overpassed [76].

- **Iron- Chromium FB:**

Iron Chromium was one of the first redox flow batteries ever invented in 1975 at the National Aeronautics and Space Administration (NASA). The redox couple used are halide solutions in both catholyte and anolyte. In the catholyte, an iron solution (Fe^{2+}/Fe^{3+}) is used whereas chromium (Cr^{2+}/Cr^{3+}) is in the negative half of the cell. The main disadvantage of this technology is the severe cross-contamination [79].

Cathode:	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E^{\theta}_{ca} = 1.00 \text{ V vs. SHE}$
Anode:	$Cr^{2+} \rightleftharpoons Cr^{3+} + e^-$	$E^{\theta}_{an} = -0.26 \text{ V vs. SHE}$
Overall reaction:	$Fe^{3+} + Cr^{2+} \rightleftharpoons Cr^{3+} + Fe^{2+}$	$E^{\theta}_{cell} = 1.26 \text{ V vs. SHE}$

Despite being a milestone itself, its commercial deployment has not been as significant as vanadium redox flow batteries. The main reason is the permanent loss in battery capacity due to the dissimilar catholyte and anolyte mean that transport of catholyte to anolyte, and vice versa [83].

- **All-Iron flow batteries:**

Aiming for cost reduction and sustainability, all iron flow batteries are the best redox flow battery system proposed as for now. Despite the numerous variations of this chemistry, the majority employ the Fe^{2+}/Fe^{3+} couple in the anolyte. The catholyte, on the other hand, may contain Fe^{2+}/Fe^{0} couple leading to a hybrid RFB configuration or the Fe^{2+}/Fe^{3+} complexed with different ligands from those in the anolyte. The exact cell voltage depends on the chemistry, but the typical range is around 0.75 – 1.2 V [83]. In Table 3 a comparison of different iron-based aqueous redox flow batteries is presented, including indicative values for performance indicators and cost, where all-iron RFB present by far the most competitive capital cost per unit of energy stored [84].

Table 3. Electrode reactions and cell performance of typical Iron-Based Aqueous RFBs. [84]

Cell type	**Electrode reactions**	**Standard cell potential (V)**	**Charge/discharge current density (mA/cm2)**	**Energy Efficiency at maximum current density**	**Maximum cycle number during test**	**Energy density / Power density**	**Capital cost (USD/kWh)**
Fe-Cr ICRFB	$Fe^{2+} + Cr^{3+} \leftrightarrow Fe^{3+} + Cr^{2+}$	1.18	40 – 160	73.9 %	60	$156\ mW/cm^2$	194
Fe-V IVRFB	$Fe^{2+} + V^{3+} \leftrightarrow Fe^{3+} + V^{2+}$	1.02	50	50.83 %	100	$23\ Wh/L$	395
Fe-Pb ILRFB	$2Fe^{3+} + Pb \leftrightarrow 2Fe^{2+} + Pb^{2+}$	0.9	40 – 120	73.5 %	26	$31\ mW/cm^2$	20
Fe-Cd ICdRFB	$Fe^{2+} + Cd \leftrightarrow Fe^{3+} + Cd^{2+}$	1.17	40 – 160	75.3 %	100	$31\ mW/cm^2$	108
All-Fe AIRFB	$2Fe^{3+} + Fe^0 \leftrightarrow 3Fe^{2+}$	1.21	40	73 %	110	$120\ mW/cm^2$	2
Zn-Fe ZIRFB	$Zn^{2+} + 2Fe^{2+} \leftrightarrow Zn + 2Fe^{3+}$	1.53	60 – 160	82.7 %	500	$676\ mW/cm^2$	100
Sn-Fe TIRFB	$2Fe^{3+} + Sn \leftrightarrow 2Fe^{2+} + Sn^{2+}$	0.9	40 – 200	78.5 %	700	$500\ mW/cm^2$	-

- **Zinc-Bromine flow batteries:**

Hybrid redox flow batteries, as opposed to pure or conventional redox flow batteries, contain at least one solid active material that is either plated or stripped within the cell. Successful exemplifications of this technology paving their way to the market are Zinc-Bromine flow batteries and Zinc-Iron. One of the main advantages of this technology is the increase in energy density due to the use of a solid metal, generally in the anode. Moreover, zinc and iron lower environmental impact are an attractive sustainable solution. However, inherent problems of plating process remain an issue, contraining independent power and energy regulation [76], [77].

A multiple number of zinc-based chemistries have been proposed for diverse battery designs over the last century. Due to the negative electrode potential in aqueous media, Zinc has been used as anode in the very first anodes designs, such as the Leclanché cell [72]. In hybrid redox flow batteries designs, the Zinc and bromide redox couple is the most widely considered and mature technology, being already in the commercialization stage [77], [85]. In this system, the electrochemical reactions can be represented as follows:

Cathode: $\mathrm{Br_2(aq) + 2e^- \rightleftharpoons 2Br^-}$ $\quad \mathrm{E^{\theta}_{ca} = 1.09\ V\ vs. SHE}$

Anode: $\mathrm{Zn \rightleftharpoons Zn^{2+} + 2e^-}$ $\quad \mathrm{E^{\theta}_{an} = -0.76\ V\ vs. SHE}$

Overall reaction: $\mathrm{ZnBr_2(aq) \rightleftharpoons Zn + Br(aq)}$ $\quad \mathrm{E^{\theta}_{cell} = 1.85\ V\ vs. SHE}$

Note that the direct reaction is the discharge, whereas the opposite process refers to the charge process. During discharge, the zinc plated on the anode dissolves in the electrolyte and becomes available for the next charging cycle [78].

The standard cell potential reached is 1.85 V at 25ºC, leading to a high theoretical specific energy of 440 Wh/kg in contrast with the real values acknowledged by current commercial systems of 60-85 Wh/kg [86]. Among other limitations, the lower current densities and lifetime of 10-14 years are some of the disadvantages when compared to VRFB, approximately 3 650 cycles in the overall lifetime [67]. The main time limitation is the non-uniform dendrite formation on the anode, being anode structures one of the main areas under development [78].

Despite this disadvantage, the LCOS can be comparable to VRFB thanks to the lower raw material costs, reaching values lower than 0.20 €/kWh-cycle [77]. Note that round-trip efficiency is approximately equal to 80%, similar to VRFB, not playing a major role in the competitivity of the technology [67].

4. Vanadium Redox Flow Batteries Characterisation

Due to the higher level of maturity [76], all-vanadium redox flow batteries will be considered as the reference technology of analysis. Vanadium Redox Flow Batteries (VRFB) utilises two redox couples, namely VO^{2+}/VO_2^+ at the cathodic side and V^{2+}/V^{3+} at the anodic side. The reactions taking place in each electrode and the consequent overall reaction are:

Cathode: $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $E_{ca}^{\theta} = 1.00\ V\ vs.\ SHE$

Anode: $V^{2+} \rightleftharpoons V^{3+} + e^-$ $E_{an}^{\theta} = -0.26\ V\ vs.\ SHE$

Overall reaction: $VO_2^+ + V^{2+} + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O$ $E_{cell}^{\theta} = 1.26\ V\ vs.\ SHE$

Note that the direct reaction corresponds to the discharge reaction, whereas the opposite one is referred to charge reaction. In this chapter a comprehensive technology review will be conducted in order to identify the operation at a system level and relevant considerations regarding safety, cost and value chain.

4.1. System description

The species are dissolved in an electrolyte solution, most commonly water based. Both electrolyte volumes are stored in external tanks and pumped through the stack as shown in Figure 20.

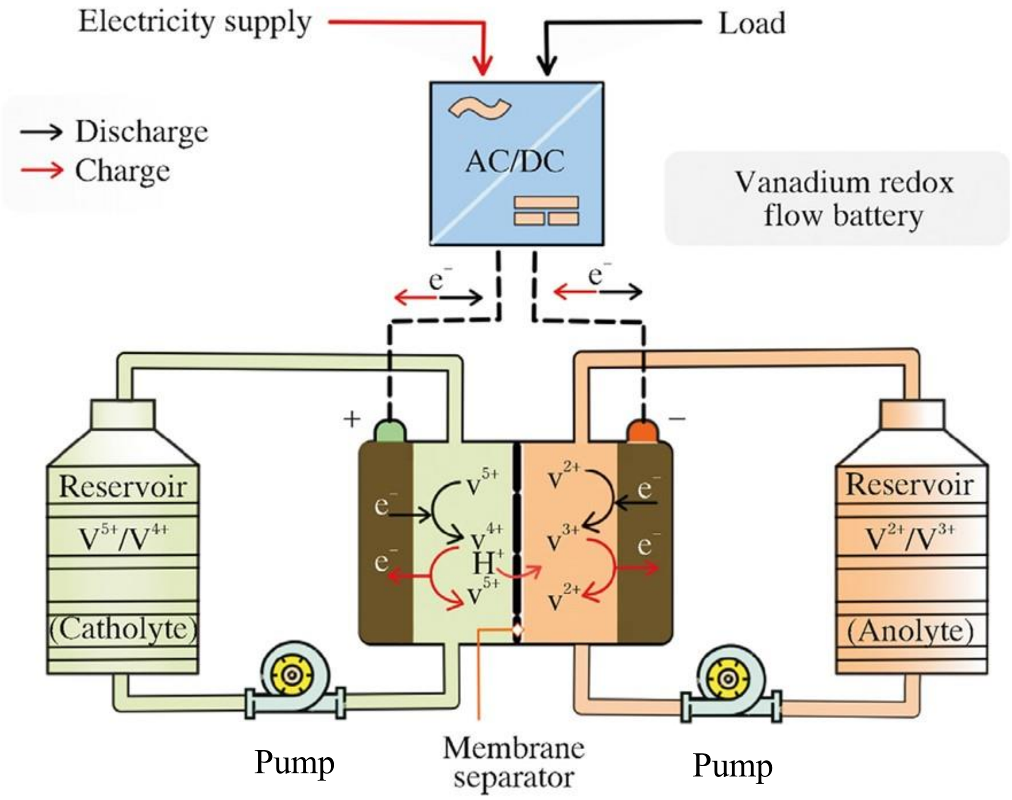


Figure 20. Schematic diagram of vanadium redox flow battery. [78]

Among the different sub-systems, the most important ones for the techno-economic analysis perspective are the ones affecting the energy balance and the good battery. Regarding to this criterion, the most relevant subsystems are electrochemical stack, hydraulic circuit and thermal management. Power electronics should be considered in the techno-economic analysis, but due to the higher efficiency of this type of devices and low dependency with the system operation, the energy losses associated will be considered constant and equal to 95%.

The main component of the electrochemical system is the stack, which is composed by cells in series, where the electrochemical reaction takes place. In Figure 21, a detailed diagram of a cell compartment can be observed. Among the main components, six are highlighted: endplates (1), current collectors (2), graphite plates (3), gaskets (4), porous electrodes (5) and the ion-exchange membrane (6).

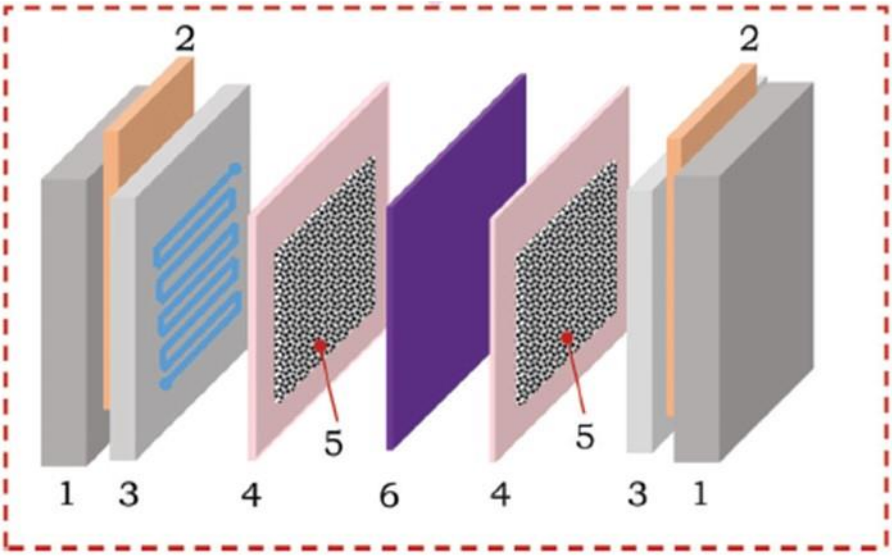


Figure 21. Detailed diagram of cell compartment in flow batteries with a flow design. [87]

The main role of endplates or bipolar plates is to bring robustness to the stack and electrically isolate with the adjacent electrode of opposite polarisation that, in case of contact, would lead to a short circuit. The series connection between the same polarisation electrodes is done by current collectors, leading the electricity towards the accessible stack connections.

Graphite plates are used to distribute the flow, which can be engraved with a serpentine flow field. By implementing flow fields, higher conversion yields can be reached, reducing electrochemical losses. On the other hand, the increase in length can lead to high pressure drops that diminish the effectiveness of the strategy in improving the stack performance. This remains an important research and development area of focus [87]. Gaskets unite graphite with the electrodes, that are usually a compressed porous electrode. The electrode porosity can also play a major role in the conversion yield and pressure drop of the electrochemical system being one of the main parameters to characterise experimentally in order to achieve realistic models [88].

Additionally, the porous topology can play a major role in the concentration losses as it affects significantly the three-phase boundary required to catalyse the reaction. Electronic charge, ionic phase and porous phase need to be in contact for the reaction to take place. If the number of these grains is reduced, the resulting probability of the three species reaction diminishes. This situation can happen if the share between solid matrix, porosity and contact with the membrane is low by design or by the concentration limit being surpassed.

Regarding the ion exchange membrane, in the case of vanadium redox flow batteries the most widespread type is Proton Exchange Membranes (PEM). Like other electrochemical technologies that use PEM such as water-hydrogen systems, ionic membranes represent the most critical element in terms of cost and maintenance in the stack, accounting for over a 55% of the materials cost in the stack [89]. Perfluorinated polymers such as *Nafion Dupont*® are the most widely used in the VRFB systems because of the chemical stability in highly oxidative V(V) environment and high proton conductivity, leading to lower ohmic resistances and overall higher efficiency [79].

4.2. Electrochemical System

The most important sub-system in redox flow batteries characterisation is the electrochemical system. Despite numerous projects, its modelling remains a challenge to solve in the upcoming decades given the complexity and numerous phenomena to consider. Aiming to comprehend the technology behaviour, the polarisation curves for different SOCs and flow rate are explored. This knowledge enables to identify KPIs and gather relevant knowledge for future BMS and EMS development.

4.2.1. Electrochemical characterisation and modelling

In a first attempt to model the dynamic behaviour of the vanadium redox flow battery, a model was developed based on the COMSOL tutorial for Vanadium Redox Flow Batteries [59], with some small variations considering the hypothesis and modifications set in literature regarding the same model [88], [90], [91]. Thanks to this model, the behaviour and understanding of the mechanisms, as well as the guidelines for modelling prospectives have been identified.

Computational Fluids Dynamics (CFD) models enable to better assess the expected behaviour of complex systems employing fluids by solving the differential equations that characterise their behaviour. This analysis is the most adequate one for vanadium redox flow batteries given the complexity and interaction between different phenomena. Among the phenomena modelled, the following are highlighted:

- Electrodes evolution reactions.
- Sulfuric acid dissociation.
- Ion transport equations.
- Donnan’s potential conditions in the membrane.
- Self-discharge reactions.

It must be acknowledged that the flow-by electrode description is agnostic to the flow field designs. The concentration profile and the performance can be highly influenced by the flow field design, being one of the open research verticals on the technology development. Moreover, the laminar assumption on the electrode description shows some limitations. Higher turbulences related to higher Reynolds numbers could lead to different results regarding the vanadium species concentration evolution as well, affecting both the cell performance and pressure drop in the stack.

Considering the relatively nascent aspect of the technology, experimental validation and characterisation of components is highly recommended. As an example, the electrode porosity effect has been acknowledged in literature to have a significant impact on the results. In Figure 22 the impact on vanadium V(II) and V(V) has been analysed for the modelled cell, being the V(III)/V(IV) concentration the complementary gradient distribution under the hypothesis of balanced cell.

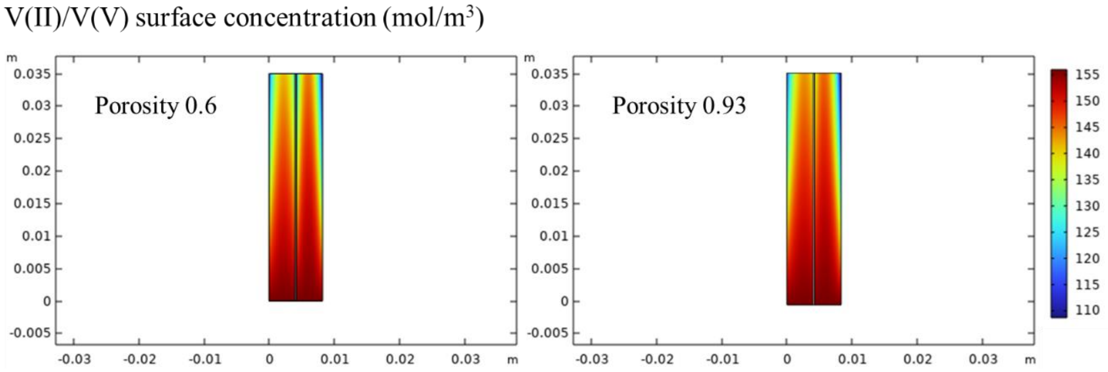


Figure 22. Comparison of porosity effect on Vanadium V(II) and V(V) surface concentration evolution.

By modifying the input flow speed, initial concentration and temperature, the model can be adapted to different operative conditions. The model has been validated by replicating the results shown in the tutorial [59]. Nonetheless, some discrepancies with measured data have been acknowledged in literature regarding the cell operation [88], [91].

The results are valid for the purposes of the project which are focused on a first estimation of the viability of the product and understanding of the phenomenon mechanisms. However, the objectives of the project do not justify a more detailed study on the interaction effect between cells within a stack and experimental validation, which can heavily influence the efficiency due to the shunt current effects, among other phenomena. For this reason, the techno-economic analysis is backed up with real measured data presented in literature. If the technology seems favourable for the company, a better characterisation endorsed by the device testing is recommended. As an example of characterisation tests to conduct in order to improve the CFD model developed are impedance spectroscopy and charge/discharge battery cycling tests [92], [93].

4.2.2. Polarisation curves

Polarisation curves are graphs that allow to estimate the cell operation in a plane conformed by cell current and voltage (I_{cell}, V_{cell}) when the cell conditions differ from the thermodynamic equilibrium. These charts present a graphical representation and comparison between the Nernst voltage or equilibrium voltage (at zero net current) and the overpotential derived from transport phenomena. In most common electrochemical systems three main regions are highlighted, named after the predominant transport phenomenon that causes the overpotential when compared to the equilibrium potential. These regions are activation overpotential, ohmic overpotential, and diffusion overpotential (Eq. 3).

$$V_c = E(T, p_i) \pm [\eta_{act}(i) + \eta_{ohm}(i) + \eta_{conc}(i)] \qquad \text{(Eq. 3)}$$

The overpotentials sign take a positive sign during the charging process, implying that a higher voltage than the equilibrium should be applied during battery charge. On the contrary, when the discharging process takes place, the overpotentials are deducted from the equilibrium potential, meaning that a lower voltage than the theoretical equilibrium is provided to the load. The difference between the overpotentials during charge and discharge is known as the charging and discharging hysteresis, which determines the round-trip efficiency of an electrochemical cell. A generic polarisation curve emphasizing on each overpotential regions of prevalence is shown in Figure 23. Note that the current density has been considered positive for charge and negative for the discharge zone. Usually, charge and discharge curves are both represented as a function of absolute current density in the positive graph region.

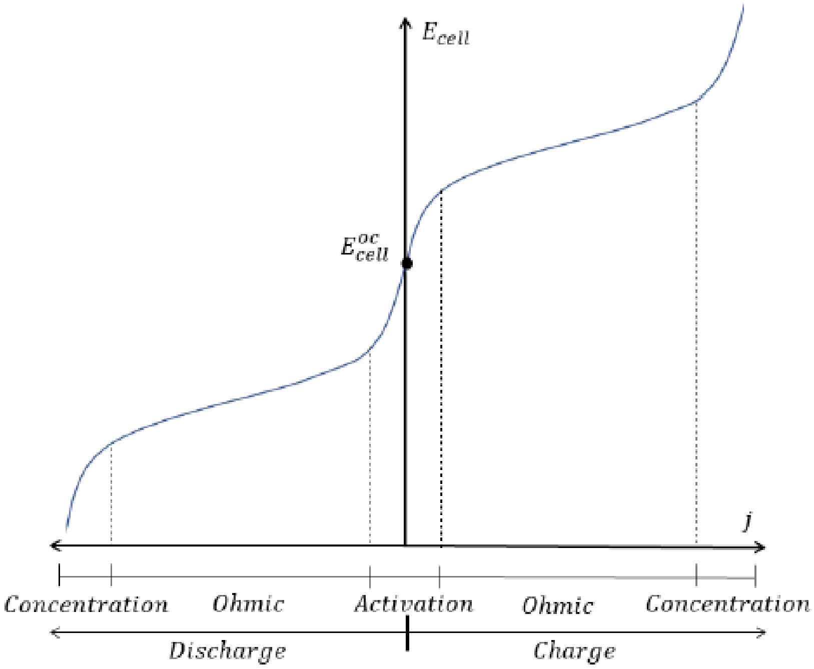


Figure 23. Generic illustration of the regions of prevalence of each overpotential in a cell. [82]

In open cells, the overpotential exclusively depends on the current density, which is directly proportional to the fuel flow rate under steady state conditions. In closed systems, the SOC needs to be considered as the composition varies through time modifying the equilibrium potential. Considering this aspect, VRFB polarisation curves also vary with the SOC, as it is directly proportional to the electroactive species concentration.

Figure 24 shows the polarisation curve associated to a vanadium redox flow cell with an active area of 2.55 cm^2, compressed by 20-25 %, a Nafion 212 separator and an electrolyte composition of 1.5 M V in 2.6 M SO_4^{2-}. The pumped flow through the cell is 18.25 mL/min and the experiments were performed under room temperature [94]. While maintaining the same current density, it can be observed that during discharge (negative slope curves) the lower the SOC (colour lines), the lower cell voltage, and vice versa for the discharging curves. Additionally, a translation along the y-axis can be spotted for different SOC as the main discrepancy between charging and discharging curves, which is reflected in the OCV variation.

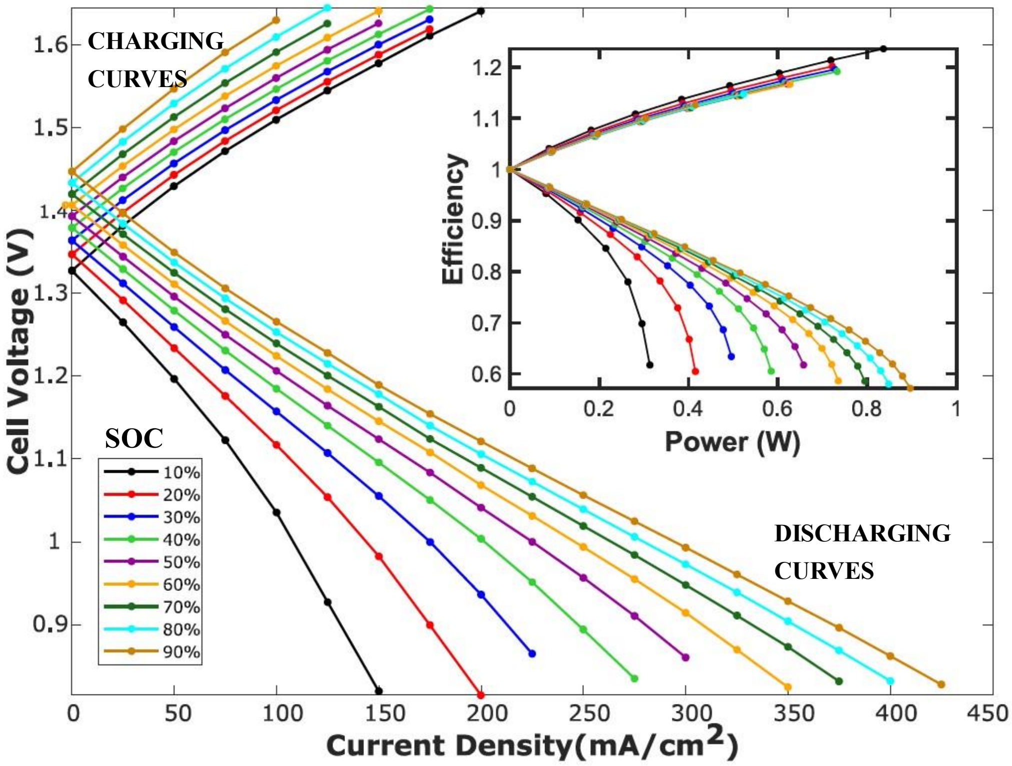


Figure 24. Polarisation curves at different SOCs for a VRFB cell. [94]

Furthermore, the efficiency defined as the ratio between the OCV minus the ohmic losses by the OCV are represented against the power. Note that this efficiency description is not valid for the charging curves. Nonetheless, it shows that the higher the power the lower the efficiency during the discharging cycle. The steep slope shows that this technology is heavily affected by the increase in current and, therefore, power. A compromise solution between efficiency and power should be considered in the BMS and EMS strategies.

The activation region is linked to the charge transfer both at the cathode and anode, noticeable at low current densities. These losses arise from the kinetics of the electrochemical reactions at the electrode and electrolyte interface [93]. In order to model this effect, the kinetic law implemented is the Butler-Volmer Law (Eq. 4a-b).

$$k_R = k_{R_{FWD}} - k_{R_{BWD}} \qquad \text{(Eq. 4a)}$$

$$I = k_R = I_o \cdot \left[\exp\left(\frac{n_{RDS}\,\beta\,F}{R\,T}\eta\right) - \exp\left(\frac{-n_{RDS}\,(1-\beta)F}{R\,T}\eta\right)\right] \qquad \text{(Eq. 4b)}$$

Being k_R the net reaction rate that can be directly associated with the current I, defined as the difference between the forward and backward reaction rate (Eq. 4a). The Butler-Volmer equation (Eq. 4b) related current to the electrodes overpotential, η. It is a function of the exchange current or equilibrium current I_0, defined as the current exchanged in the electrode under equilibrium conditions and dependent on the type of reaction, temperature catalyst and active surface. Additionally, the number of electrons transferred in the rate determining step, n_{RDS} that in this case is equal to one and the symmetry factor β. According to most literature, this value was considered 0.5 leading to a symmetric behaviour between the cathodic and anodic current component.

The Tafel equation is often used under the hypothesis of low activation overpotential as due to the linear relation between the net exchange current and activation overpotential, which is valid for the activation region. As it can be deduced, the exchange current only depends on the type of reaction and the quality of the electrode. Moreover, temperature impact on kinetics can be easily deducted from the expression.

The ohmic region is linked with the charge migration, both ionic and electronic. The electronic effect is associated to the contact resistances between the bipolar plate and electrode, as well as the external electric circuit. On the other hand, the ionic ohmic losses are associated to the ionic transport through the membrane [93]. Most commonly, the electronic effect is neglected as long as the electric circuit is not extremely long. This assumption is acceptable as the electronic resistivity is around an order of magnitude higher than ionic conductivity in proton exchange membranes. In the model, only the membrane diffusivity was considered.

Lastly, the diffusion region is predominantly controlled by the mass transport phenomenon. At high current densities, the molecular diffusion in the electrodes might not be fast enough to replace the molecules reacting leading to a saturation of the electrode. The mass transfer limits the maximum current that can be obtained in the system considered. Considering Fick’s law, this effect is linked with the binary diffusion coefficient, porosity of the porous medium and its tortuosity. Its representation is already embedded in the Nernst Law definition (Eq. 1), as the activation is referred to the bulk concentration of species.

4.2.3. Hydraulic System

In literature, the main efficiency drop is associated with the hydraulic system and the power required for electrolyte transport, reducing in some cases the overall energy system efficiency to 70% [61], [66], [95]. Despite mechanical losses increase when the pumped flow increases, the battery capacity increases (Figure 25). This leads to the need of a compromise solution between the flow rate and pumping power consumption, considering the overall system energy efficiency.

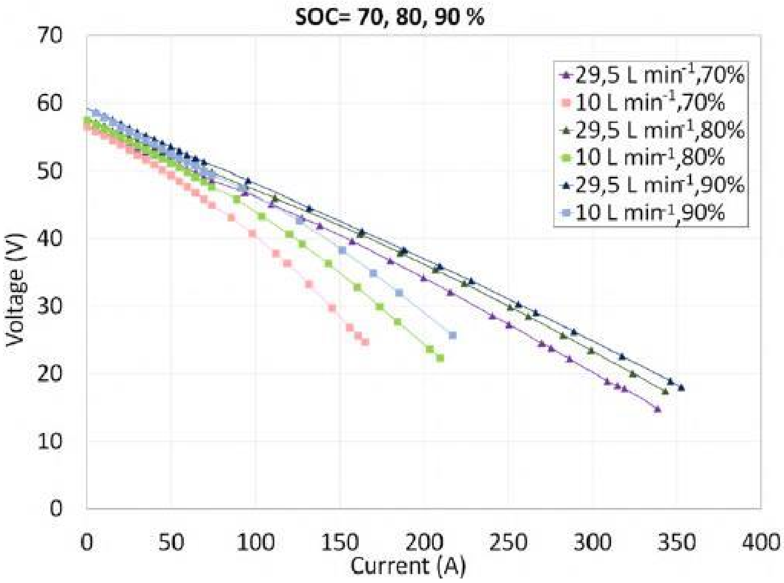


Figure 25. Experimental polarization curves for a stack for different flow rates and SOC. [81]

In literature, these modifications are usually measured by a dimensionless number expressed as the ratio between the real flow rate and the minimum theoretical flow rate (Eq. 5).

$$\lambda = \frac{Q_{real}}{Q_{th}} \qquad \text{(Eq. 5)}$$

Theoretical flow rate depends on the instantaneous current, vanadium concentration and minimum state of charge considered during operation (Eq. 6). Further optimisation of the flow rate should be implemented in the models. In literature, an optimum between 6 and 9 is used as a reference [96].

$$Q_{th} = \frac{I(t)}{z_F \; c_V \; SOC_{min}} \qquad \text{(Eq. 6)}$$

In order to model the hydraulic system, the pipelines scheme should be considered. Given the level of detail required by the on-site design, this value could vary between different installations. Therefore, a conservative estimation will be implemented taking literature estimations as a reference pressure drop differentiating between the cells and the distribution circuits from the tanks to the power modules as well as inside the modules distribution (Table 4) [81], [97].

Table 4. Pressure drop estimation per equipment and circuit. [81], [97]

Description	**Pressure drop (bar)**
Pressure drop per stack	0.28 bar
Pressure drop per module circuit	0.2 bar
Pressure drop per circuit tank to module	0.3 bar

Another focus of research is the characterisation of electrolyte, especially density and viscosity given the impact of this properties in the expected pressure drops and, therefore, in the overall system efficiency. The main factors that affect density and viscosity are temperature and the electrolyte composition. For a given molar concentration, the SOC can be considered as an indirect measurement of the concentration of species, leading to a better online characterisation of the properties evolution during cycling.

Regarding density, the first trend that can be spotted in both posolyte (V^{IV}/V^{V}) and negolyte (V^{II}/V^{III}) is the temperature dependency (Figure 26), where lower temperature tends to imply a higher density.

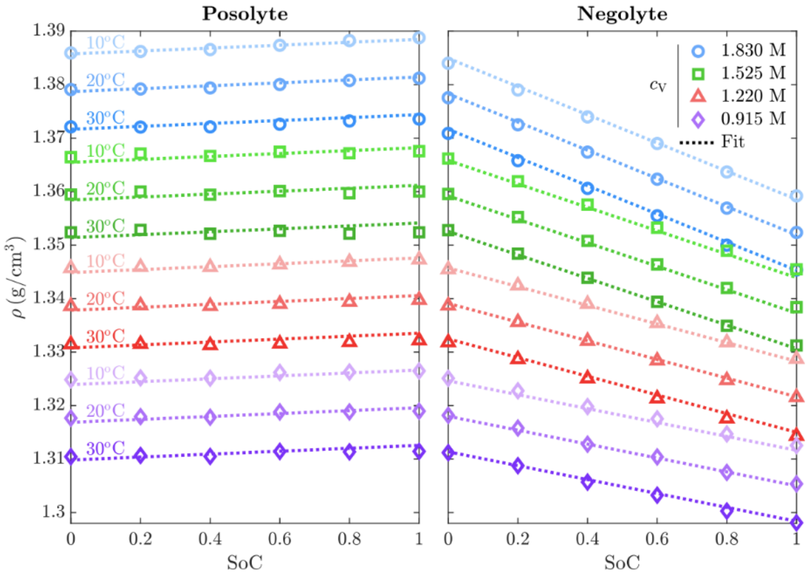


Figure 26. Electrolyte density variation in both the posolyte (left) and negolyte (right) for different vanadium concentrations, temperature and SOC. [98].

The relationship between overall solution vanadium concentration seems to be the opposite, as the lower the concentration the lower the density asit is represented by different colour curves. Moreover, the dependency between density and SOC seems to be negligible in the posolyte, while in the negolyte a pronounce decline is observed when the SOC increases.

Viscosity shows a similar dependency with overall vanadium concentration and SOC evolution (Figure 27). The higher the concentration, the higher the viscosity leading to an increase in the pressure drop in the hydraulic circuit and, therefore, the increase of auxiliary power consumption [98]. Nonetheless, higher vanadium concentrations are preferred as the energy density is significantly improved. The negolyte seems to also have a higher dependency on these factors when compared to the posolyte.

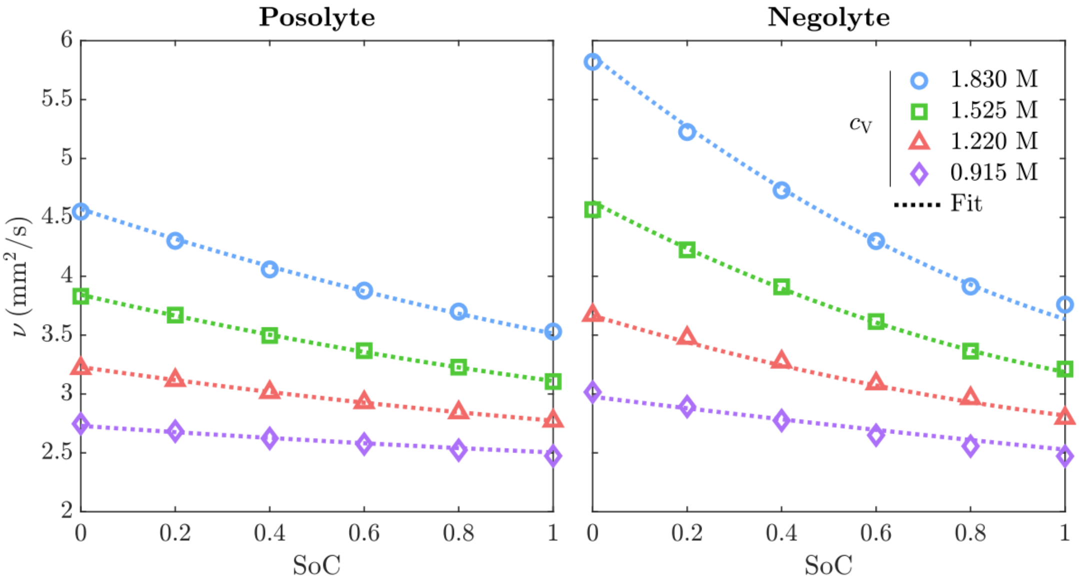


Figure 27. Viscosity evolution for different SOC and vanadium concentrations in the mix for posolyte (left) and negolyte (right) at 20 °C temperature. [98].

4.2.4. Thermal Management System

Thermal management is a crucial part of battery modelling and controlling, no matter the typology considered. In electrochemical batteries such as LIBs, safe charge and discharge windows are highly dependent on the good thermal conditions in order to avoid undesired and dangerous effects such as active material deposition and explosion that could risk human safety [95].

Despite temperature control and monitoring being extremely important in flow batteries due to the impact on the electrolyte properties, is not common to include thermal management systems in models [81]. For flow batteries, the main heat sources are:

- Exothermic discharge and self-discharge reactions.
- Endothermic charge electrochemical reaction.
- Pumping system heat transfer.
- Ambient temperature and radiation.

Regarding the endothermicity and exothermicity of the reactions taking place in the VRFB, the discharge reaction is exothermic leading to an increase in temperature, as well as the self-discharge unwanted reaction. On the other hand, the charge reaction is endothermic [81], reducing the temperature and therefore reducing the safety concerns that arises with LIB batteries fast charging. The impact of this heat source is often neglected given the low heat rate and the flow dissipation effect, unlike closed system batteries.

Despite the safety enhancement, the charging time is limited by the efficiency of the process as the concentration losses are significant at high current densities as well as the pump energy demand. Additionally, in industrial applications the low temperature of operation and almost negligible heat generation avoids the use of the residual heat for process heat.

Thermal energy losses transferred from the pumps could also be included, but are also neglected in most models. For this reason, the most important heat source to consider is the ambient temperature in order to determine the installation location for techno-economic analysis.

A compromise temperature range between performance and system durability needs to be reached. The optimal range for vanadium redox flow batteries is estimated to be between -5 – 50ºC [61], [66]. Nonetheless, a conservative approach to reduce precipitation risk will be considered limiting the electrolyte temperature within the 10 - 40ºC range. An active heat management system is required in order to maintain the safe operation of the stack between these ranges, accompanied by the inherent energy losses. The temperature lower limit is linked with the solubility of $VOSO_4$, vanadium (IV), whereas the upper limit is associated with the precipitation of V_2O_5, vanadium (V), at higher temperatures [79], [99]. Electrolyte composition modifications have led to increase the initial temperature window of 10-35ºC, to -5 to 60ºC ranges for other chemistries, reducing the need for electrolyte control in most areas of the world [67], [79].

Locations where the ambient temperature oscillates between this range are preferred as the thermal requirements are lower, reducing the auxiliary energy demand and, therefore, costs. In this case, the location considered needs to fulfil the temperature requirement and high solar irradiance, which is a valid hypothesis for Spain. The higher irradiance implies a lower LCOE in PV assets, that has boosted a significant allocation of self-generation plants. It is expected that the number of congestion points rise first in these areas as the VRE share is expected to increase at a faster rate, favouring the implementation of energy storage systems as previously discussed.

4.3. Efficiency

Additionally, efficiency is one of the most important factors to study considering the Efficiency First Principle [100]. The definition of efficiency in electrochemical systems can vary depending on the focus of the study. At system level, the main efficiency definition is the overall energy efficiency that considers all of the system losses. The main losses associated to the system as well as the influencing factors are identified in Table 5.

Table 5. Main losses in VRFB and influencing factors. [101], [102].

Losses	Definition	Influencing factors
Pump system losses	The energy losses associated with the pump system operation.	Flow rate, pump design, pump efficiency, converter efficiency.
Hydraulic loss (pressure drop)	Energy losses due to the pressure drop in the hydraulic system.	Pipelines distribution, shape of distribution channels, pipes and manifolds.

Thermal management loss	Energy losses of the cooling and heating system.	Electrolyte temperature, ambient temperature, VRFB system design, battery housing design
Ohmic loss	Power losses due to the transfer of charge ions such as ions and electrons.	Internal resistance, current density, electron and ion transportation resistance.
Crossover loss	Capacity losses due to the diffusion of vanadium ions causing a capacity fade.	Membrane permeability of vanadium ions.
Mass transport loss	Vanadium ion concentration loss due to the mass transport of active species.	Low electrolyte velocity, low vanadium concentration in the solvent.
Activation loss	Loss associated to the activation of the electrochemical reactions both at the cathode and anode.	Kinetics of the vanadium redox reactions.
Shunt current	Current caused by conductivity of electrolyte and non-zero electrical field potential gradient.	Conductivity of the electrolyte, number of cells, the shape of channel and pipes, internal resistances.

Usually, the pump system and hydraulic losses are combined into the same term given the relation between them. On the other hand, the sum of ohmic, crossover, mass transport, activation and shunt current losses are usually referred to as electrochemical losses given its origin. Last but not least, thermal management losses are associated with the energy consumption required for both cooling and heating of tanks in order to avoid active material precipitation. Compared to hydraulic and electrochemical losses,

When considering the balance of the plant, the major auxiliary consumption is assigned to the anolyte and catholyte pumps. Given this reason, the round-trip efficiency of vanadium redox-flow batteries is heavily affected by the charging and discharging times. The longer the storage periods, the lower the losses associated with auxiliary services. On the contrary, frequent charging and discharging can severely affect the round-trip efficiency and be detrimental to the overall system performance [76]. In cases where the combination of both requirements is simultaneous, hybrid cases considerations with short-term energy storage as suggested as a good alternative to improve the overall system efficiency and cost, among other complementary characteristics and advantages [75].

4.4. Safety

Safety concerns are rising importance, especially when it comes to emerging technologies. Social acceptance is also one important piece of project management and attracting potential customers. Considering the Electrochemical Stability Window (ESW), redox couple within the water stability window are considered as less dangerous given the lower fire hazard when electrolytes are in contact with air moisture, enabling the use of aqueous electrolytes [76]. However, the energy density will be decremented by the voltage difference reduction. Organic based redox flow batteries that allow to use a wider ESW between electrochemical species is one of the researching develop strategies.

Another factor that can heavily affect safety are operating temperature. The operating ambient temperature range of VRFB is usually between 5 °C and 50 °C, whereas the range opens up to − 15°C and 50 °C for Zinc-bromine flow batteries [67]. Maintaining these temperatures requires a thermal management system in order to avoid undesired effects, especially considering the internal reactions exothermicity and endothermicity. Nonetheless, the requirements are less strict for VRFB than LIBs due to the role that the thermal management plays in both. Whereas in VRFB it is oriented towards the long-term conservation of the device, in LIBs the inferred hazards of thermal runaway can lead to safety issues.

4.5. Vanadium value chain

Existing vanadium value chain involves five main steps mainly focused on vanadium electrolyte manufacturing (Figure 28). Currently, the main cost incurred in VRFB is vanadium electrolyte [103], being the main component understudied in this chapter. Nonetheless, other components manufacture such as proton exchange membranes contribute significantly to the cost and should be monitored.

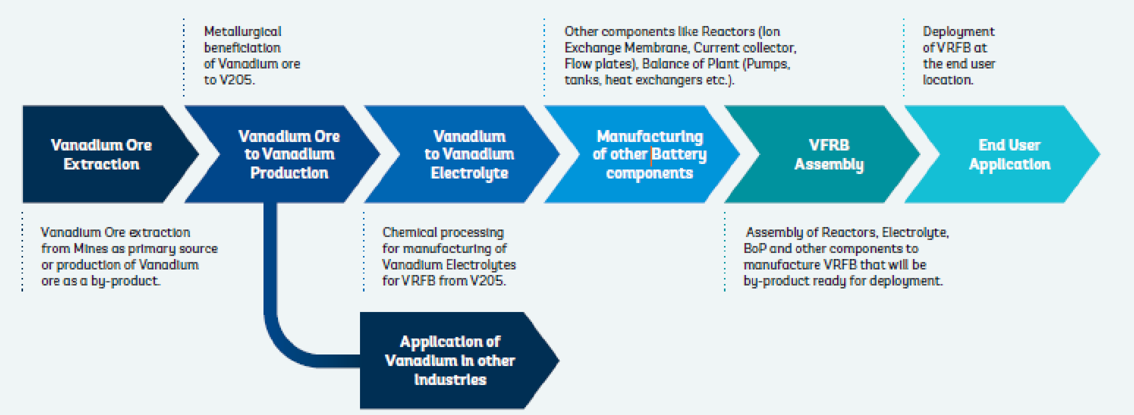


Figure 28. Existing vanadium value chain for Vanadium Redox Flow Batteries production. [103]

According to the fifth list of Critical Raw Materials (CRMs) for the EU dated in 2023, vanadium is a critical raw material as it has been since 2017. The methodology followed to determine CRM consider both economic importance and supply risk in order to determine which materials are critical for European strategies. In the case of vanadium, the major global supplier is China in the extraction stage accounting for 62% of the global supply. Far from an even geographical distribution, the remaining vanadium production is localized in Russia (20%), South Africa (11%) and Brazil (8%) [104]. Some reserves have been localised in the USA and Australia [103], but projects have turned not to be so relevant as for now.

EU import reliance cannot be calculated as there is no production and trade for vanadium ores and concentrate in the EU, being 100% import dependent [104]. One of the reasons is the strong link between extraction and production sites due to the low vanadium concentration found in nature [105], which further increases the transport costs if concentrations are not clustered on-site. For this reason, the extraction and production concentration are the main concern for the European Union. Note that among the selected uses in the CRM analysis, battery production is not on the list, whereas high-strength-low-alloys for i.e., aeronautics, space and nuclear reactors, as well as chemical catalysts, are the main activities considered [104]. The evolution of the mentioned industries could incur in a direct competition for the materials.

This unequal geographical distribution has led to a high price volatility. This is one of the main concerns in the technology development due to the uncertainty associated. The value has oscillated between almost 2 to 29 USD/lb (around 4.12 and 60 €/kg) in the latest 25 years, as it can be observed in the time evolution for vanadium pentoxide flakes (Figure 29).

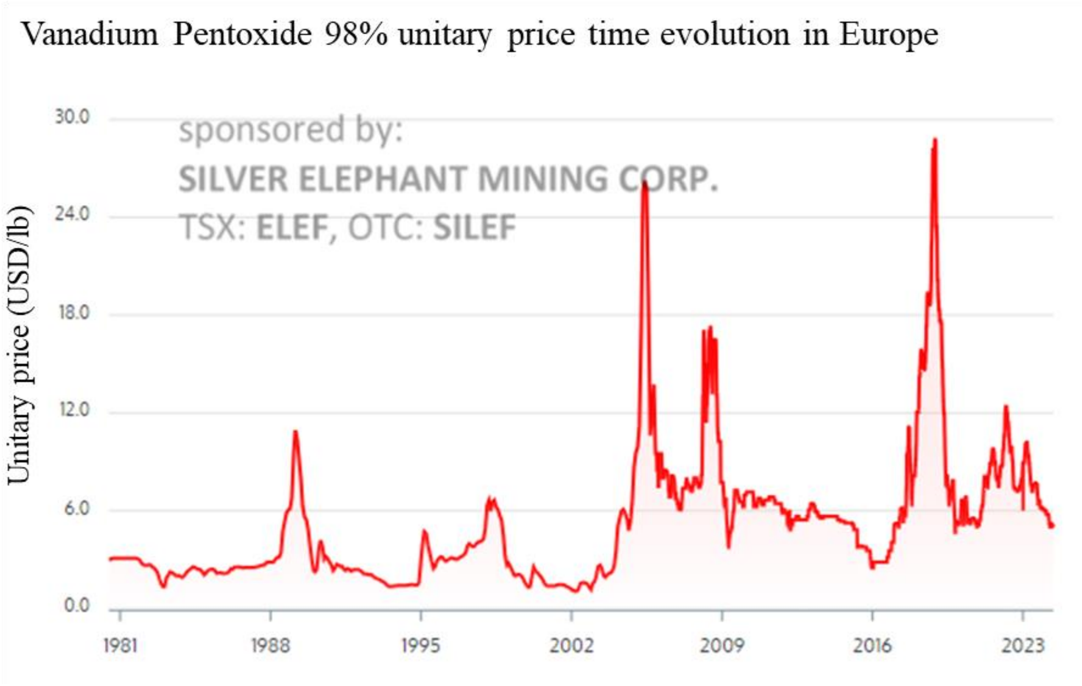


Figure 29. Vanadium Pentoxide Flake 98% price time evolution in Europe. [106]

Vanadium production is often divided into three categories: primary production produced from its ores by salt- roasting, water leaching, filtration, desilication and precipitation, accounting for 18% of global vanadium supply in 2020; Secondary production from fly ash, petroleum residues, alumina slag and recycling of spent catalysts used in crude oil refining, accounting for 10% of global supply in 2020; And co-production slag in iron ore processing for steel production, being the major source in 2020 with 72% of the global supply [103]. Due to the lack of vanadium mineral ores and crude oil reserves in the EU, the possible routes for its provision are co-production by incentivising steel production industries in line with the REPowerEU plan [11] or recycling and/or reprocessing of vanadium from Vanadium Electrolytes (Figure 30).

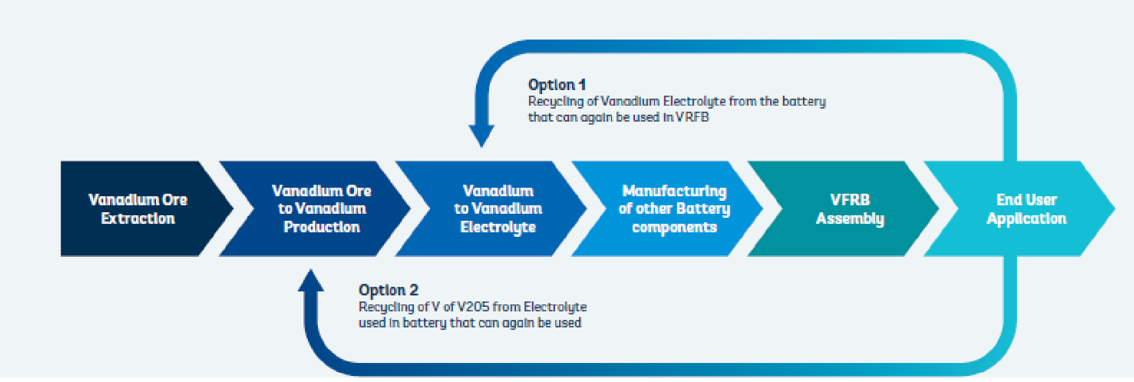


Figure 30. Recycling of Vanadium in the VRFB Value Chain. [103]

Considering vanadium recycling itself, recyclability of the material is considered to be easily regenerated and given the cost impact more worthwhile than conventional batteries [76]. However, the scale needs to be considered and it plays a major role when making economically feasible the recyclability of strategic materials due to the facility investment required in conventional batteries. This aspect is not so significant for redox flow batteries due to the easiness to re-adapt vanadium redox flow batteries. Periodic electrolyte remixing, electrolyte transfer and electrochemical rebalance are highlighted measures to reduce the capacity fading [79].

Despite these techniques increasing the CAPEX and Operational Expenditures (OPEX) in the system [79], they could lead to a never-ending energy storage medium, being the perfect option for long engineering projects at large scale such as Transport Systems Operators (TSOs) at a regional level. In this sense, the stack device would be the major factor limiting the cycle life.

Most commonly, two techniques are employed: electrochemical and chemical recycling. The former is considered a strategy to re-balance concentration between electrodes by applying a controlled charged cycle. The cost associated with this measure are mainly the energy required and it can be considered as part of the O&M costs due to the required frequency of the measure to maintain the capacity of the battery. This expenditure can be optimised in terms of costs by conducting it during high renewable share periods.

Chemical treatment is referred to the addition of chemical components required to maintain the good performance of the battery. Depending on the electrolyte composition and possible impurities found through the operation of the device, the additives may differ, but no complex substances are required. For this reason, this procedure is not considered complex and can be directly performed on-site.

4.6. Environmental footprint

Sustainability focus is one of the main areas to consider in the development of energy systems throughout the whole value chain. In terms of ecological assessment, the estimated 100-year global warming potential of battery technologies is highly improved when using redox flow batteries, especially due to the lifetime increase. Another factor that improves the environmental footprint of redox flow batteries in general is the decoupling between energy and power outputs prevents the unnecessary material consumption due to oversizing in output power or capacity [76]. The impact estimates are approximately 0.04 and 0.03 kg CO_2 eq. by kWh-lifetime for VRFB and Zinc-Bromide respectively, whereas lower than 0.01 kg CO_2 eq. by kWh-lifetime is estimated for iron flow. The reason why iron flow presents a clear advantage in this sense is associated with both lifetime and most importantly lower emissions associated with iron mining. Lithium-ion batteries, on the other hand, suppose 0,13 kg CO_2 eq. by kWh-lifetime [67].

When considering battery manufacturing, energy and water demand needs to be considered. Vanadium stands for the most energy intensive manufacturing process, 1.45 MJ/kWh-lifetime, followed by an approximate 1 MJ/kWh-lifetime of lithium ion and 0.40 and 0.05 MJ/kWh-lifetime of zinc-bromide and iron flow [67]. This indicator should be as low as possible considering the efficiency first principle, but the impact on carbon emissions can be limited considering the use of carbon-free energy sources in the manufacturing. A more critical aspect would be water use, where lithium-ion accounts for the highest estimated use of 0.85 kg water by kWh-lifetime versus 0.03; 0.01 and lower than 0.01 kg water by kWh-lifetime for Zinc-bromide, vanadium and iron flow [67].

Table 6. Estimated environmental comparison of main redox flow batteries and LIBs. [67]

	VRFB	**ZnBr**	**All-Fe**	**LIBs**
100-year global warming potential (kg CO_2 eq. by kWh-lifetime)	0.04	0.03	<0.01	0.13
Energy demand during manufacturing (MJ/kWh-lifetime)	1.45	0.4	0.05	1
Water use (kg water/kWh-lifetime)	0.01	0.01	<0.01	0.85

Redox flow batteries present ecological advancements when compared to other electrochemical batteries for the use of conventional containers, mostly made of plastic. Nevertheless, the use of vanadium, requires a safe containment due to the negative impacts of its environmental release, increasing the recyclability costs of the storing medium containers [76].

4.7. Vanadium alternatives

Research efforts are currently focused on reducing equipment and maintenance costs, as well as searching for new electrolytes systems for higher energy densities [76], [79]. In the stack size, electrode optimisation for higher performance, membrane development and electrical system development are highlighted [76].

Nowadays, All-vanadium redox flow batteries seem to be the most widely used technology. In this study, it will be considered given the higher TRL, as well as the long-life expectation. However, the next redox flow batteries chemistries should be considered as prospective solutions in case that the KPIs surpass the VRFB performance. The next trends on redox flow batteries and associated benefits are summarised in Table 7.

Table 7. Next trends in redox flow batteries. Own elaboration based on data from [78], [85], [99], [107], [108]

Technology	
Zn-Br	Second most mature technology. Discarded due to the lower lifetime expectations.
All-Fe	Discarded due to lower maturity and lack of literature. Prospective interest due to low environmental footprint.
Quinones	Low TRL and number of demonstration plants as for now.
Organic-based	Promising trend that could enhance VRFB technology by increasing the ESW and, therefore, leading to higher energy densities [80].
Hydrogen-vanadium redox flow cell	Enhancement on round-trip efficiency for hydrogen for reversible fuel cells and reduces cost-dependency on vanadium price [99]. It could be of interest in a scenario where hydrogen economy is boosted.

5. Industrial sector characterization

Given the diversity of sectors requirements, context and parameters, the most optimal solutions for industrial and specifically heat decarbonisation can heavily differ based on the case considered. There is no silver bullet solution when it comes to the industrial sector decarbonisation, requiting a holistic perspective to identify the most suitable technology for the context considered [109]. The most common energy carriers demanded are electricity and heat, which will be the focus of the project.

5.1. Industrial decarbonisation

Numerous solutions are available to address industrial processes decarbonisation, often categorised into four main types: efficiency improvements, energy source switching, emissions capture, and material inputs change (Figure 31) [109]. The former aims to promote the better use of resources, ensuring the same level of quantity and quality while reducing the material and/or energy inputs to the system. These techniques vary in terms of complexity, cost, and effectiveness. For instance, upgrading machinery technology may involve substantial costs and lengthy payback periods, whereas adjusting operational variables to achieve greater efficiency may yield similar resource optimization at a significantly lower implementation cost depending on the case [18]. Nonetheless, these actions should be prioritised, as efficient energy and material utilization not only represents the cleanest alternative, but also carries significant cost impact on other abatement techniques downstream due to their largest role in curving energy demand and emissions in the upcoming years [24], [100].

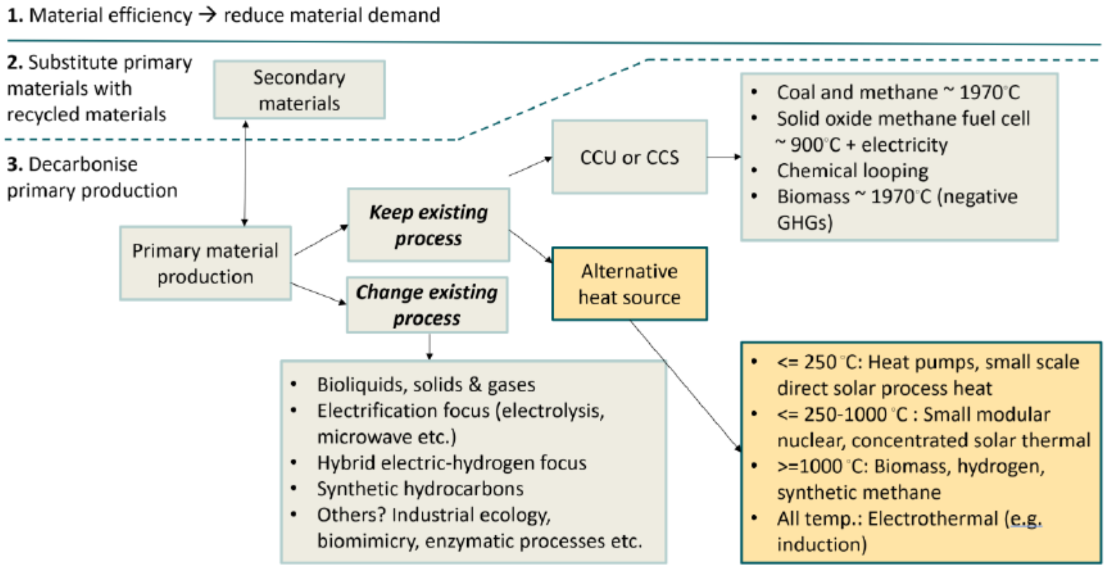


Figure 31. Flow chart for choosing the most suitable industrial decarbonisation options. [109]

The energy sources shift can either entail a change towards less carbon-intensive or even net-zero energy vectors. An example would be the fuel transitioning from coal to methane, as the associated emissions per unit of energy produced is reduced given the lower carbon content per unit of releasable energy by combustion. However, this approach still shows some drawbacks, including exposure to price volatility typical of fossil-based energy sources and energy dependence based on resources geographical availability. The optimal solution to tackle both challenges effectively lies in transitioning to renewable energy sources.

Another approach to reduce emissions involves the implementation of capture technologies. These technologies are based on the capture of emissions and pollutants, such as sulphur dioxide, particulate matter, and nitrogen oxides, to name a few [51], [110]. Depending on the process and according to the local legislation, pollutant removal systems must be implemented to prevent significant environmental disruption. In this note, Carbon Capture Use and Storage (CCUS) is gaining attention for stationary applications.

CCUS can be retrofitted to existing power and industrial plants to capture carbon emissions while maintaining the same equipment. This technology has the potential to decarbonise hard-to-abate sectors where process electrification is not feasible due to high temperature requirements or inherent process emissions. Additionally, CCUS can be coupled with sustainable biomass sources, leading to negative emissions [111], [112]. On the other hand, cost remains a barrier to the widespread adoption of this technology at the necessary pace to achieve the Net Zero Scenario by 2050 [23], where carbon pricing plays a significant role in its economic feasibility considering current regulatory framework [113]. Increased research and development efforts are required to address this disadvantage, particularly considering the different TRL among available technologies [114]. Although this alternative might be conceived as a postponement of the inevitable energy transition as the use of fossil fuels is perpetuated [115], the net zero goals might not be achieved on time without their deployment [24].

An emerging technology based on a similar concept gaining popularity is Direct Air Capture (DAC). The technology is based on capturing CO_2 emissions directly from air, allowing for the removal rather than avoidance of CO_2 emissions. However, CCUS technologies as operate with stationary and highly concentrated CO_2 flows should be prioritised due to the lower energy requirements and, therefore, the better use of energy and materials [115].

The last, but not least tactic to reduce carbon emissions is changing material inputs. A notable example is the production of green ammonia. Ammonia production conventionally relies on natural gas as a feedstock for hydrogen production via Steam Methane Reforming (SMR), accounting for over 70% of ammonia production worldwide as for 2020 [21]. In the case of polygeneration plants requiring a carbon source, alternative carbon sources can be considered such as biomass and waste recovery. Note that good practices are crucial to avoid unintended consequences such as compromising food crops and reversing the waste hierarchy [116]. Material efficiency and implementation of circular economy principles should be prioritized as initial actions to reduce both CO_2 emissions and waste production throughout the product lifecycle [117], [118], [119].

5.2. Energy demand profiles

There are different energy use cases depending on the energy reservoirs available and the demand requirements, naming heat-to-heat, heat-to power, power-to-heat, power-to-power and power-to-X protocols [69]. In the scope of the project, power-to-heat, power-to-power and power-to-X will be highlighted as they are the ones that better suit the electrification processes:

- Power-to-heat: Electricity is converted into heat, which is stored and later released as heat.
- Power-to-power: Electricity is stored and then used as electricity. If a TES system is implemented, said electricity is converted into heat, stored, and later converted back into electricity.
- Power-to-X: electricity is converted in something else, named “X”, that can be used as an energy vector. Some examples of these protocols include ammonia, Sustainable Aviation Fuels (SAF), and steel.

Electrical, mechanical and electrochemical energy storage is usually linked to power-to-power energy storage use profiles. The energy system segment services for Behind-the-meter applications ranges time-of-use energy cost management, maximising self-consumption, power quality, uninterrupted power supply and limitation of upstream disturbances [76]. Note that depending on the technology considered, if either energy is stored as electricity or thermal energy, the number of conversions differ from one case to other. This factor can heavily affect the overall efficiency of the energy system and can affect the predominance of one technology over the other one depending on the application profile.

5.3. Heat electrification.

The main challenge industry presents are heat electrification, given the wide temperature range process heat requirements (Figure 32), conversion costs, competitiveness risk, and desired long facility life, among others [109]. As mentioned before, for very low technologies water tanks thermal energy storage is the preferred technology implemented.

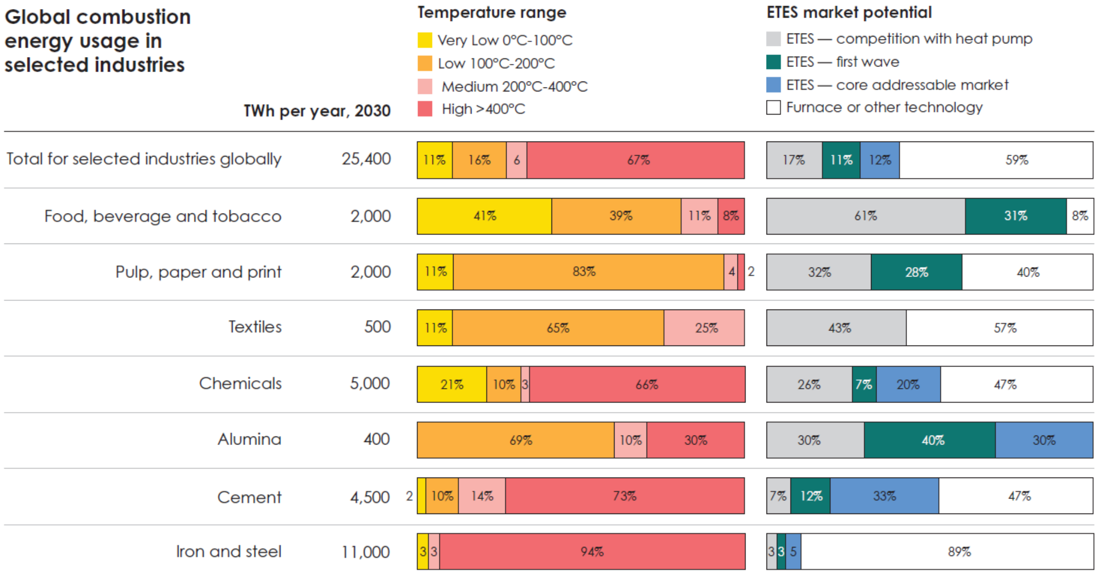
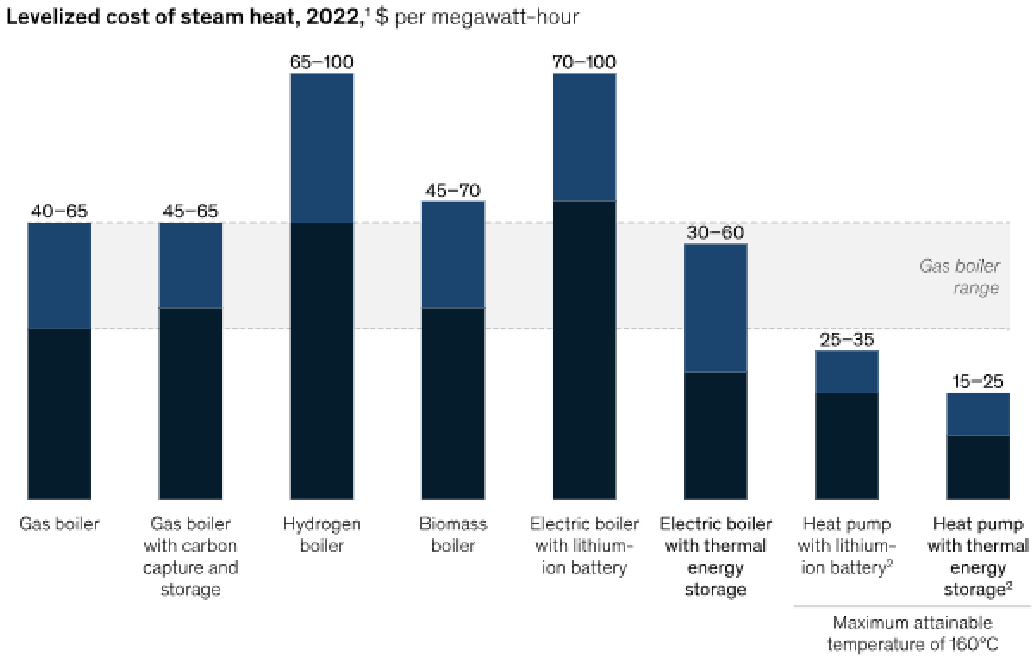


Figure 32. Overview of market segments in global market sizing estimate in selected industries. [25]

In industrial processes, steam and hot air applications are highlighted as the most common forms of heat used. In power to heat applications, the levelized cost of delivering medium-pressure steam using TES can be cheaper than conventional gas boilers and other low-carbon solutions (Figure 33) [38], when coupled to industrial heat pumps and electric boilers.



¹Ranges reflect representative fuel prices: gas ($6–$12/mmBTU), electricity ($25–$50/MWh), biomass ($200–$350/t). In the hydrogen boiler case, hydrogen production costs amount to $2.1–$3.2/kg of hydrogen.
²High-temperature industrial heat pump.

Figure 33. Levelized cost of medium-pressure steam heat for a 2022 basis. [38]

Despite the need of further research and development on this area, there are currently available technologies that could help decarbonise and electrify the lower temperature heat demand (Figure 34). The TRL, however, can heavily differ from one temperature range to other as well as different applications. Regarding heat pumps, as one of the most promising electrification technologies in industry, up to 100ºC are commercially available and established on industry. As the temperature rises, technological complexity increases leading to prototype status and technology development on the temperature range 100-140ºC. Higher than 140ºC are still on the laboratory research and proof of concept phase [70].

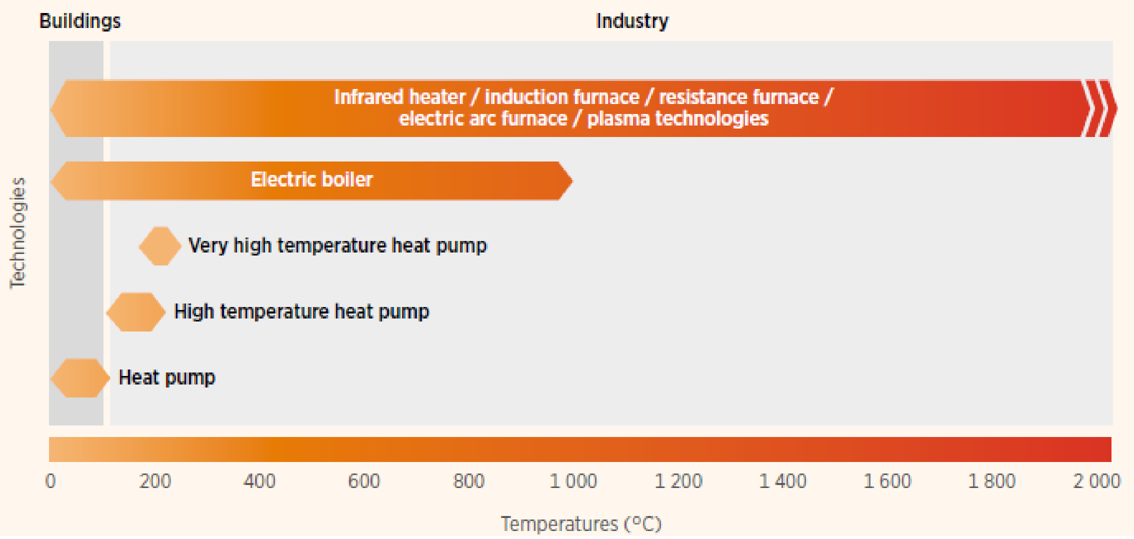


Figure 34. Temperature ranges and electrification technologies for industry sector. [70]

Electrifying heat technologies include [26]:

- Industrial heat pumps.
- Electromagnetic heating.
- Electric furnaces.

All of the above technologies' enhancement should be monitored in order to assess which energy storage technology could be better suited as the energy demand will be significantly affected. Despite the prospective advantages of these technologies, the heat electrification considered in order to develop a technology agnostic comparison case will be an electric furnace via the Joule Thompson effect. The estimated efficiency for transforming electricity into heat by these means is usually considered a 99%.

5.4. Case description

The user profile is identified as one of the most important factors that may influence the prevalence of one LDES technology over other according to experts. Considering this reason, the understudy case implemented is the most beneficial application considering vanadium redox flow batteries main advantage: power and energy decouple.

The energy profile in an industry can heavily vary depending on the process requirements, which are usually divided into continuous and batch processes. Whereas continuous processes require uninterruptible energy source, batches process can vary the energy and power demand requirements as the main steps operate discontinuously [120].

The temperature range considered is between low and 400 ºC, contemplating the technical aspects of the company TES product as benchmark. Further analysis could be considered in other industrial sectors, such as food and beverage manufacture where batch production is frequent and the percentage of process heat in the selected temperature range is even higher than the one considered in general (Figure 32).

In this case, the chosen industrial sector selected is the chemical sector given the simultaneous production of different product batches. This variation heavily dependent on the production quantity and type has been identified as a prospective early adopter of vanadium redox flow batteries as energy storage carrier. Authentic data provided by a participating company has been used as a reference. Due to confidentiality agreements, the specific name of the company cannot be disclosed. All analysis and findings presented herein are based on this genuine data, allowing for a comprehensive and realistic exploration of the research question.

The industrial case considered produced simultaneously 4 different chemical species non-disclosed and the energy demand is process steam. The batch process requires a different steam demand in each time interval (Figure 35). The day considered for sizing and modelling the system is the least favourable day, which in this case would be the peak demand. A previous step has been the identification of this trend by data polishing.

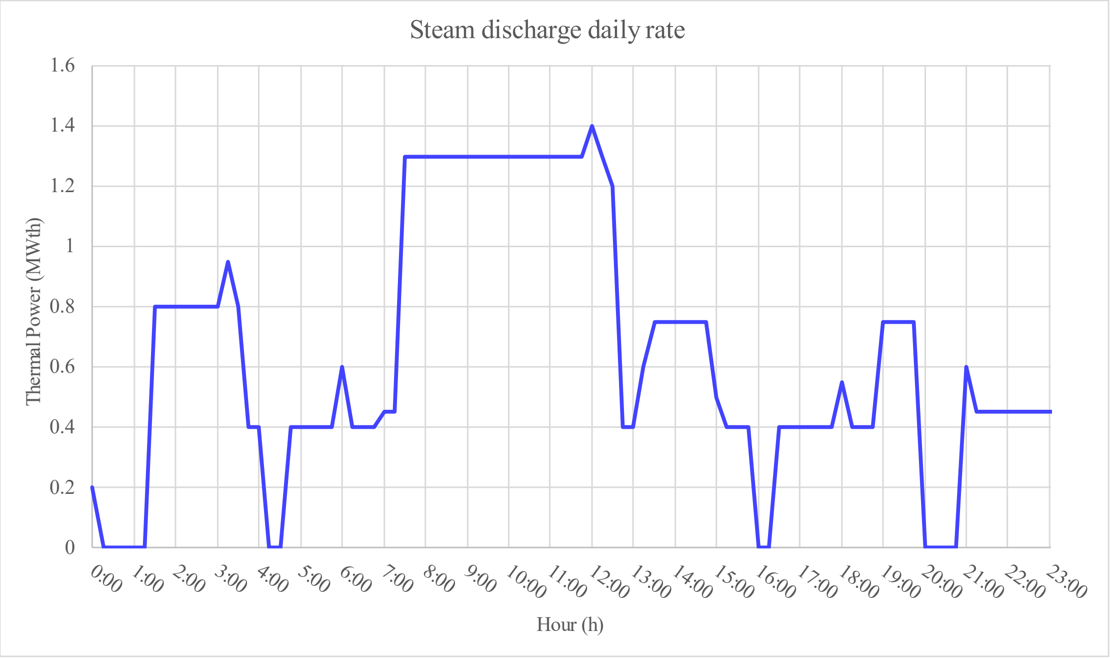


Figure 35. Aggregated daily steam peak demand. Adapted from consumer data.

In this case, the peak demand takes place during weekdays in winter, reaching a steam demand of 1.4 MWth. The measured time step in the profile is 15 minutes, value that can be used in the system modelling. This time step is large enough to cover the transient effects on the model and simplify the model if required for further BMS and EMS development.

The daily thermal energy demand is over 60.65 MWh in the design day, whereas the peak thermal power is estimated to be around 1.4 MW. Considering a 99% Joule-Thompson efficiency in the conversion from power to heat and inverter efficiency of 95%, the electricity demand can be calculated as summarised in the below table (Table 8).

Table 8. Industrial electricity power and energy demand in the design day.

Daily Electricity Demand (MWh/day)	Peak Power Demand (MW)
61.263	1.414

Note that these values are referred to the net daily demand in the peak demand day. However, electricity prices could favour a higher energy and power demand if the daily electricity prices vary significantly throughout the day, or the ancillary services are highly paid. In this case, the energy storing capacity has been set to 14 hours to harmonize the results with the modular equipment of the company's current product.

5.5. Flow battery Sizing

In terms of sizing, power and energy decoupling can lead to different optimal sizes depending on the overall case description, especially electricity prices profiles. In this case, in order to diminish the possible discrepancies in the assessment for financial estimations, the energy and power are sized considering similarities in the company's product sizing criteria to better compare them.

As previously mentioned, the main advantage of redox flow batteries is the decoupling between energy and power sizing. Power is sized by selecting the number of cells considering a design voltage and current. In order to calculate the power, the maximum gross power required needs to be calculated. The power scheme considered (Figure 36) corresponds to the VRFB discharge in the peak power demand for the end-user.

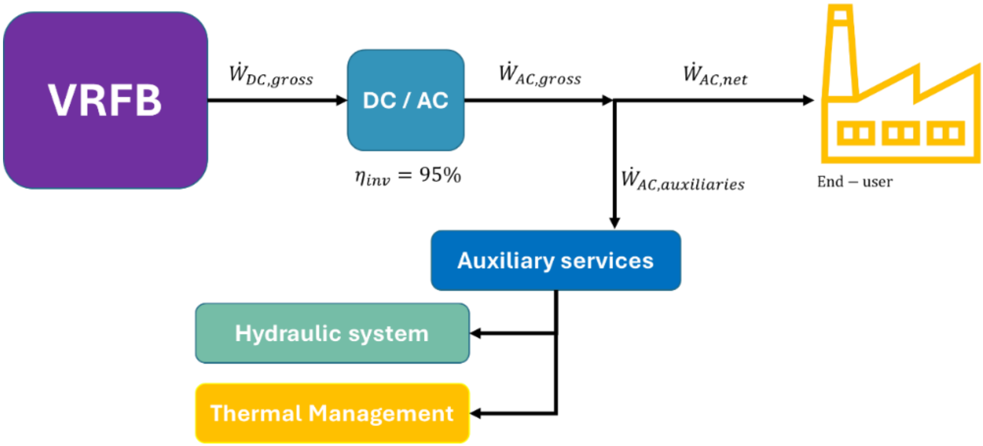


Figure 36. Power flow scheme for VRFB discharge case.

The gross power is defined as the power produced by the VRFB without considering the power converter losses and auxiliary services consumption, that would satisfy the end-user power demand. The auxiliary services demand depends on the power sizing, being considered for sizing purposes only an initial estimation of the overall system in 75%, according to most literature considered, including the inverter efficiency. This conservative approach slightly oversize the system, allowing a more reliable performance in the worst operating conditions in terms of power. Considering the 99% of electricity to thermal conversion, the power flows distributions are as shown in Table 9.

Table 9. Power flow distribution for sizing.

Thermal Power End-User	1.489	MW
AC Power, net	1.504	MW
AC Power Losses	0.644	MW
AC Power Gross	0.107	MW
AC Power for Auxiliaries	0.537	MW
Gross DC Power	2.148	MW

The gross DC power is obtained, which is linked with the voltage, current and number of cells by the Eq. 7.

$$P = N_{cell} \cdot P_{cell} = N_{cell} \cdot V_{cell} \cdot i_{cell} \cdot A_{cell} \qquad \text{(Eq. 7)}$$

Deciding a design reference potential for vanadium redox flow batteries can be challenging and introduce biases on the results considering the steep slope of the polarisation curves for highly concentrated solutions. In this case, it has been considered a $\mathrm{VOSO_4}$ concentration of 1.6 M and a $\mathrm{H_2SO_4}$ concentration of 2 M as it established as the highest concentration in literature that enables a safe and durable operation. The reference design voltage considering the polarisation curves is 1.092 V and the current density 120 $\mathrm{mA/cm^2}$, considering as a reference the curve for maximum flow rate, equal to 29.5 L/min and 70% SOC [81], [121]. Considering the lack of references in literature regarding this sizing criteria, further sensibility analysis should be conducted in order to better assess the impact of the hypothesis considered in the overall product competitivity. In this case, it has been considered a 70% SOC and the maximum current during discharge to enable the device to run as much as the industrial case requires during the peak power demand.

Another problem regarding vanadium redox flow batteries is the lack of performance information at a large-scale level in literature. Most of the data available and studies are based on lab scale experiments, which are less sensible to scale-up effects such as the importance of shunt current losses associated with the membrane area increase. Considering this limitation, in this project the performance considered will be based on the largest active area study validated experimentally at a pilot scale in order to obtain a better understanding of the real performance of vanadium redox flow batteries [81]. The relevant stack parameters are summarized in Table 10. Nevertheless, further research on larger electrodes should be conducted in order to validate the effectiveness of the technology.

Table 10. Relevant stack sizing parameters considered. [81], [121].

Electrodes area	600	cm^2
Number of cells per stack	40	
Temperature	20	℃
Discharge current density	120	mA/cm^2
Charge current density	100	mA/cm^2
Voltage limit per series line	488	V
Maximum SOC	90%	
Minimum SOC	10%	
Safe Margin	10%	

Considering the inverter voltage limit, the number of stacks in series per inverter are calculated. This stack line will be connected in parallel with other stack lines, following the modular design observed in commercial applications, such as the SUMITOMO product. Considering these factors and rounding down in order to fulfil the voltage limit criteria, the number of stacks in series per power invertor equals 8, developing around 0.025152 MW per stack series line under design conditions. The number of stack series lines in parallel equal 79.7, which will be approximated to 80 in order to have an even distribution of the stacks per module and avoiding uneven flow distribution due to the asymmetric piping design (Figure 37). The consequent total number of modules equals 10, which corresponds to a total active area of 1 536 cm^2.

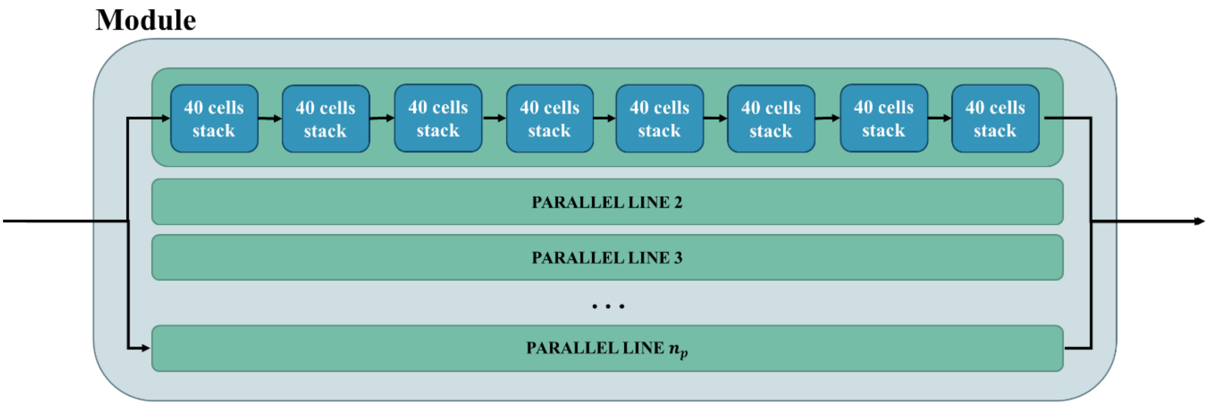


Figure 37. Connection scheme implemented for one module.

The charge and discharge duration of most common redox flow batteries usually range from 2 to 12 hours [67]. However, the possibility of additionally storing extra electrolytes tanks can be explored in order to increase the timespan, although it will heavily reflect on the cost and footprint [122].

In the case considered, the design energy capacity equals to 14 MWh, which corresponds to roughly 7 hours of storing capacity. Considering this value and the concentration of vanadium in the electrolyte mix, the volume required can be estimated. First, the energy stored in the battery is computed according to Eq. 8, a combination of the energy and capacity definition considering Faraday's Law.

$$V = \frac{E}{\overline{\mathrm{OCV}}\,(SOC_{max} - SOC_{min})F\ z_F\ M_v} \qquad \text{(Eq. 8)}$$

The average OCV, $\overline{\mathrm{OCV}}$, has been computed considering discharging curves at maximum flow rate approximate to 1.359 V per cell. In this case, the possible SOC limits range from 10 to 90%. Note that despite a complete depth of discharge is possible, it is recommended to operate within this limit. F corresponds to the Faraday's constant, $\mathrm{z_F}$ to the number of electrons transferred equal to one and $\mathrm{M_v}$ the concentration of vanadium in the electrolyte. The overall volume required for one electrolyte considering a safe margin of 10% recommended in literature equals 330.345 $\mathrm{m^3}$. This number should be multiplied by two to consider the volume required for the overall system. In this case, the number of tanks and integration criteria has considered the one implemented in already running pilot plants of similar size. Concretely, the plant considered is the one built in California by San Diego Gas & Electric and Sumitomo Electric accounting for 2 MW and 8 MWh. In the pilot plant it can be observed that 2 tanks have been installed per 2 modules, being the total number of tanks equal to the number of modules, being both numbers an even number [123]. Considering this implementation, it has been assumed that 10 tanks could be installed, serving each pair of electrolyte tanks to two modules connected symmetrically. Moreover, the study of this plant has been able to validate that the number of modules is consistent with the power required. Finally, the volume per tank rounds up to 33.035 m^3.

The tank geometry can vary from manufacturer to manufacturer. In the break dawn of VRFB commercialization, many designs are being proposed in order to improve KPIs such as energy density and overall system efficiency. Design can play a major role in the energy density of the plant as the tank sizing and systems distribution affect the overall footprint of the system. Modular designs are proposed as a mean to standardized the design and lowering costs and footprint. A common arrangement is the situating rectangular electrolytic tanks together and the stacks located above the two tanks. This configuration is often associated with 1 kW or less power systems. The Energy-Power ratio (E/P) can be still tailored by increasing the length of the tanks [122].

In this case, both the rectangular and cylindric tanks have been computed in order to estimate the best integration. For the rectangular design, the width and length has been estimated by the Sumitomo Electric product in 1.2 m and 16 m, respectively per tank [122]. On the other hand, a height limitation of 6 m considering typical values for cylindrical tanks. A diameter of 2.7 m has been considered in order to leave some void volume to absorb volume variations due to change in properties. The cover gas in these cases is usually nitrogen as an inert gas. The footprint and height per tank is summed up in Table 11.

Table 11. Tank geometry footprint and height comparison.

	Rectangular	**Cylindric**
Footprint per tank	19.2 m^2	5.73 m^2
Height	1.72 m	5.77 m

No surprise the best integration in terms of footprint for the size was cylindric as the implemented in the similar size pilot plant. Therefore, cylindric tanks will be considered due to this advantage. Nonetheless, if lower power and energy is demanded, the modular design might be a better solution for lowering the costs.

6. Technoeconomic analysis

The goal of this chapter is to develop the tools required to compare vanadium redox flow costs and benefits against the current company product, under the same conditions and context. The financial indicators chosen are the initial investment, Levelized Cost of Storage (LCOS) and Total Life-Cycle Cost (TLCC). LCOS is a better option when comparing alternative technology types through their complete lifetime cycle. Nevertheless, CAPEX and TLCC will be highlighted given the necessities of the targeted customer segment.

6.1. Initial Investment

The main financial metric considered by BTM users is the initial investment. Commonly, the initial investment is associated with the CAPEX given the tight relationship between them. In order to calculate this value, the common approach is a bottom-up analysis considering the individual costs of the required equipment, as represented in Figure 38. The level of detail can vary from project to project, considering further equipment such as additives in the electrolyte composition. The approach taken in the discretisation of the elements has considered a generic description with a conservative approach to cover the hypothesis considered. The results have been validated with literature data for similar power and energy capacity in a European context.

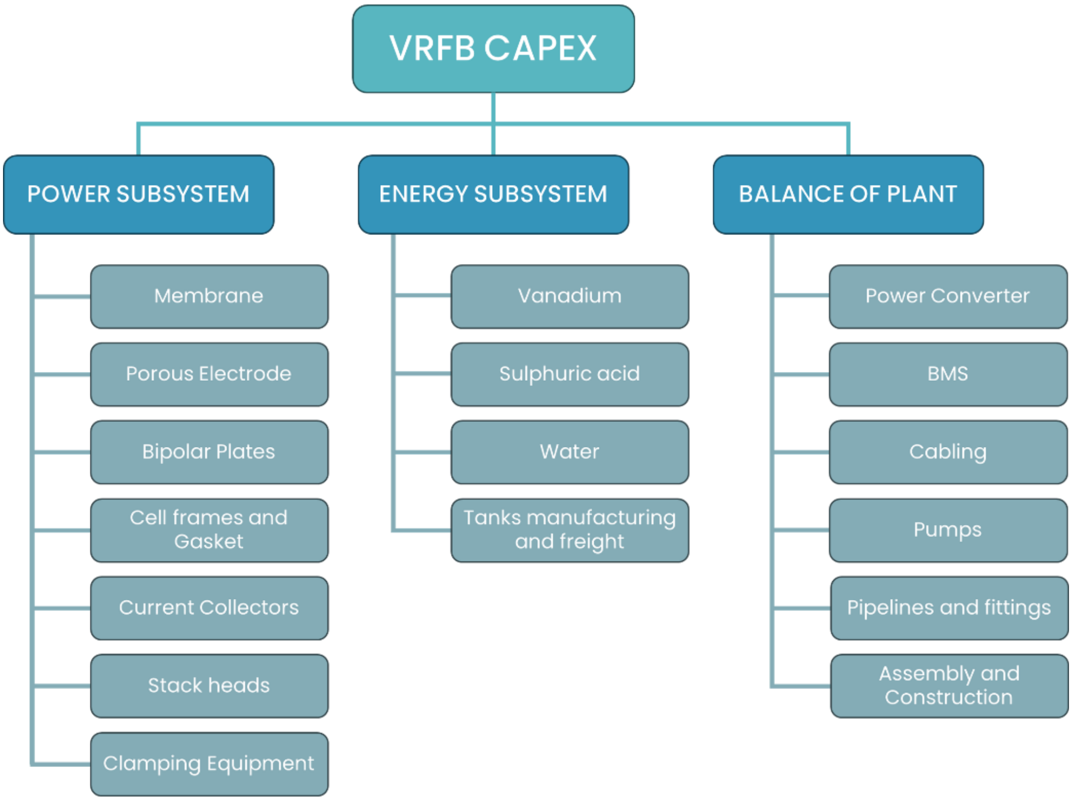


Figure 38. Detailed technical system definition of VRFB. Own elaboration inspired on [76].

6.1.1. Power sub-system

The power block cost has been estimated based on the unitary costs of each element in the stack, including the membrane cost c_M, porous electrode c_{PE}, bipolar plate c_{BP}, cell frame and gaskets c_{ffg}, current collector c_{cc}, stack head c_{sh} and clamping equipment c_{ce}. Considering the number of elements required of each component, the total cost per element has been computed (Table 12).

Table 12. Cost description per element in the power sub-system.

Description	Symbol	Value	Units	Element cost
Membrane [97]	c_M	400	€/m^2	614.4 k€
Porous electrode [97]	c_{PE}	60	€/m^2	92.16 k€
Bipolar plates [121]	c_{BP}	100	€/m^2	153.6 k€
Cell frame and gaskets [121]	c_{ffg}	150	€/m^2	230.4 k€
Current collectors [121]	c_{cc}	170	€/m^2	261.12 k€
Stack head [121]	c_{sh}	1 000	€/unit	160 k€
Clamping equipment [121]	c_{ce}	200	€/unit	16 k€

Note that the active area per cell is lower than the convenient one for a MW-application. Still the reason of choosing this cell area was due to the availability of a complete analysis on the stack behaviour at a relatively high active area. This approach constitutes a good approximation to quantify the active area required. Bigger cells have been reported in literature in a commercial state, but due to the lack of experiment results available, this cell area has not been implemented. In order to reduce the effect on the technoeconomic analysis, the number of stack heads and clamping equipment referred in literature per stack has been computed per parallel line. Excluding clamping equipment that is computed once per parallel line, the number of stack heads required per parallel line equals two. The rest of the components are expressed per active area, so no correction is necessary.

The final cost associated with the power system is approximately 1 527 680 €, which corresponds to a 1 173.31 €/kW cost based on the VRFB net power output. This value is in the range estimated by the European Association for Energy Storage (EASE), which approximates a CAPEX per power unit between 500 and 1 300 €/kW [124].

The cost distribution in the stack by element is represented in Figure 39. The values are coherent with the literature consulted.

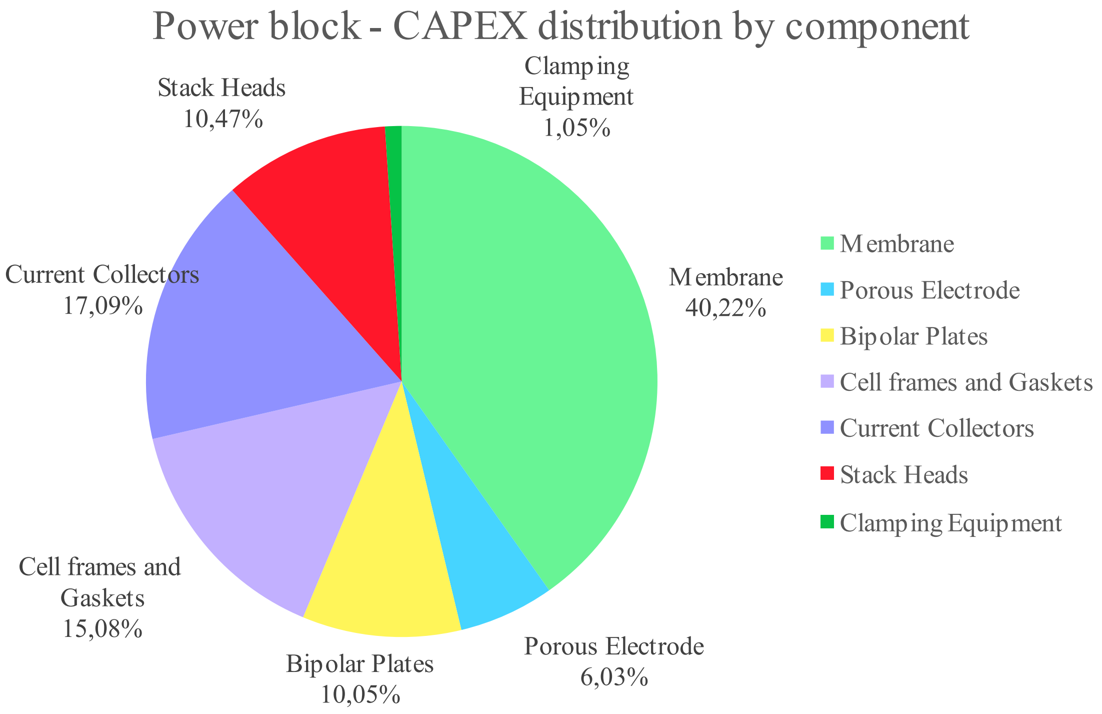


Figure 39. Power block initial investment distribution by component.

6.1.2. Energy sub-system

For the energy block, both the tank and the electrolyte costs need to be estimated. The tank cost is often estimated by a unitary cost per volume, which has been considered equal to 300 $€/m^3$ [121]. The electrolyte composition, on the other hand, has been divided into each component in order to better assess the variation of the components cost as vanadium price volatility was one of the main risks identified in the technology spread. Considering the molarity and molecular weight of the components, the mass can be calculated. The electrolyte composition and cost are expressed in Table 13.

Table 13. Electrolyte unitary cost and weight considered per element.

Component	Unitary Cost (€/kg) [97]	Weight (ton)
$VOSO_4$	20	86.156
H_2SO_4	0.05	64.8
H_2O	$1.7 \cdot 10^{-3}$	301.134

Finally, when computing the total cost of the electrolyte approximated to 1 726 880.67 €, being the unitary cost of electrolyte equal to 5 227.50 $€/m^3$. Summing up both tank and electrolyte costs, the CAPEX associated to the main energy components ascends to over 1 825 984,27 €. The cost distribution by element is strongly dominated by vanadium pentoxide cost, followed by the tank and the rest of components being almost negligible (Figure 40).

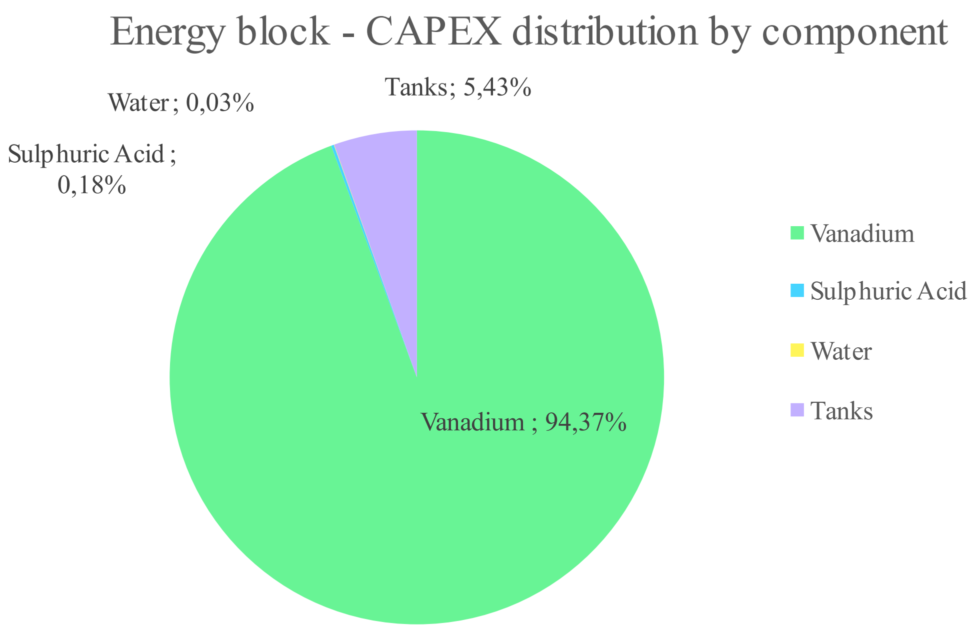


Figure 40. Energy block initial cost distribution by element.

6.1.3. Balance of the plant and power electronics

The balance of the plant includes equipment as the pumps and BMS controller, as well as cabling, pipelines and fittings. The power converter system and cabling price unitary cost is referred to the VRFB rated power. In the case of BMS the unitary cost is corrected considering economies of scale by an interpolation exponent, α, established the cost with the VRFB rated power as stated in Eq. 9.

$$\frac{C}{C_{ref}} = \left(\frac{P}{P_{ref}}\right)^{\alpha} \tag{Eq. 9}$$

Where subindex "ref" designated the reference parameter. Pipelines and fittings cost can be described as a function of pipe length as a first approximation. For a MW-scale techno-economic analysis, the pipelines cost considered pipelines made of steel and coated with PTFE, which unitary cost was estimated as 300 €/m. Considering a conservative approach, a factor of one is considered for the fitting costs, leading up to 600 €/m. The length assumed for the supply line from the tanks to the cell of each electrolyte circuit was considered 30 m in the corresponding reference, as well as an addition of 5 m of pipeline per stack and circuit [97]. Considering that each pair of electrolyte tank will supply 2 modules, an additional length of 5 m was considered per tank, summing up 35 m per tank. Additionally, the number of stacks required by circuit has been estimated up to 15 m per parallel line.

Pumps unitary cost is referred to the volumetric flow, being over 22-64 $€/(m^3/h)$ for centrifugal steel and PE pumps used in MW-size VRFB [97]. Considering a conservative approach, the highest limit has been chosen as reference. The number of pumps is two per module, considering the highest flow rate as the reference for the unitary cost. The flow rate per pump can be estimated multiplying the maximum volumetric flow rate per stack by the number of stacks in the module, leading to 226.56 m^3/h of electrolyte.

Finally, the heat exchangers need to be sized in a preliminary study to consider the cost associated with the stack. It has been estimated an effective transference area of 53 m^2 based on similar offers for plate heat exchangers. The area is quite low when compared to other applications thanks to the low thermal demand required by the system in the location selected and the high approach that characterises this heat exchangers, ranging from 3 to 5 °C. It is recommended that this value is updated for other locations, as the thermal demand might significantly change and reduce the viability of the project.

Lastly, the assembly and construction costs associated to the installation have been estimated as a percentage of the CAPEX obtained by the sum of the components. All of the parameters discussed are summarised in Table 14.

Table 14. Techno-economic analysis parameters considered for balance of the plant.

Component	**Cost**	**Unit**
Power Converter System [121]	150	$€/\mathrm{kW}$
Pumps unitary cost [97]	64	$€/(m^3/h)$
BMS reference cost $(C_{ref}/P_{ref}^{\alpha})$ [121]	800	$€/\mathrm{kW}^{\alpha}$
BMS interpolation exponent [121]	0.76	
Cabling [97]	4	$€/\mathrm{kW}$
Pipelines and fittings [97]	600	$€/\mathrm{m}$
Plate Heat Exchangers [97]	180	$€/\mathrm{m}^2$
Assembly and construction [97]	20	% CAPEX

Considering the CAPEX required for both the energy and balance of the plant costs, the CAPEX per unit of energy storage equals 308.65 €/kWh, which is within the EASE cost range of 100 – 400 €/kWh. The total CAPEX defined as the sum of all the costs previously described equals 5 851 596.60 €. This value is aligned with the CAPEX reference for a similar power and energy capacity value in literature in a EU-member country [97]. The overall CAPEX distribution by element can be observed in Figure 41, being the electrolyte mix the most significant cost.

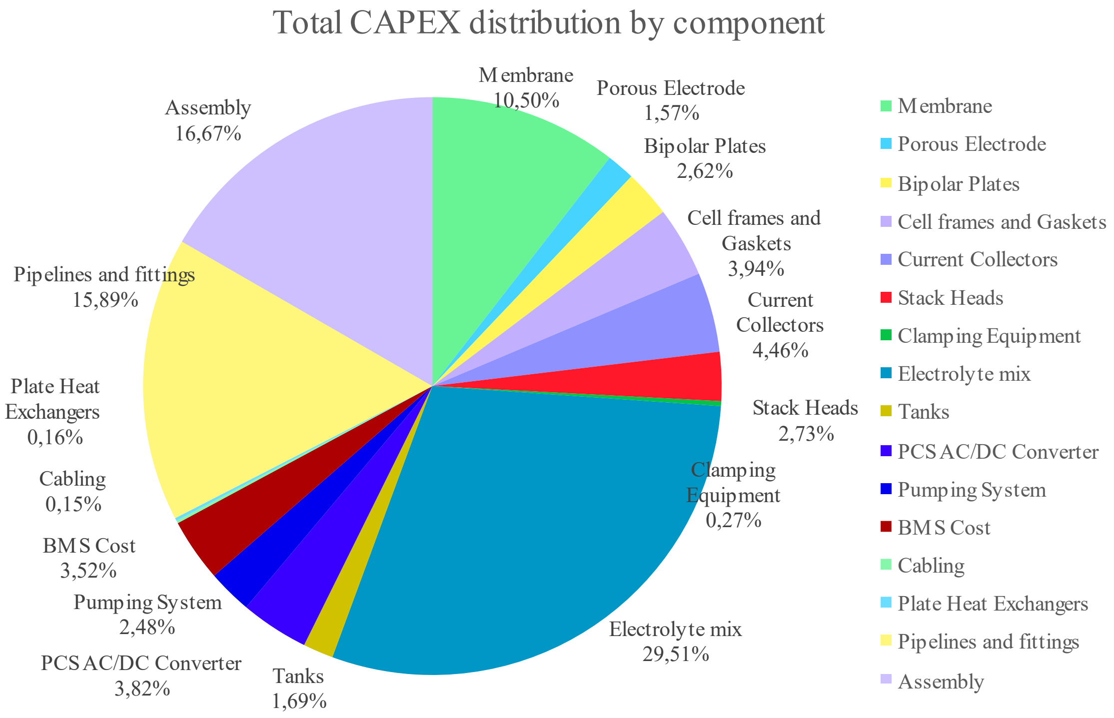


Figure 41. Overall system CAPEX distribution by component.

6.2. Total Life-Cycle Cost

Total Life-Cycle Cost is defined as the incurred costs though the ownership of an asset over the investor's period of interest [125]. As regards energy storage technologies, the costs incurred can be estimated as the sum of the CAPEX and the levelized costs incurred for operation and maintenance (O&M), energy supplied during charging and the End-of-Life (EOL) cost (Eq. 10).

$$TLCC = CAPEX + \sum_{n=1}^{N} \frac{O\&M}{(1+i)^n} + \sum_{n=1}^{N} \frac{E_{ch}\, c_{Ec}(1 - n \cdot deg)}{(1+i)^n} + \frac{C_{EOL}}{(1+i)^{N+1}} \qquad \text{(Eq. 10)}$$

In this case, the analysis period of interest will coincide with a project lifetime of 20 years. In order to compute this value, a cash flow analysis will be conducted. The approach will consider the cashflows incurred in each year depending on both the costs and revenues. The cashflows account for the money value variation through time. The annual capacity degradation will have an impact on the energy charged.

Table 15. Summary of financial parameters and values considered.

Financial Parameter Description	**Value**
Project lifetime, N [125], [126]	20 years
Operation time per year, $\mathbf{t_{op}}$	8 169 h
Capacity Factor, CF	93.25%

Weighted Average Cost of Capital, WACC [127]	3.25%
Internal rate of return, i	10 %
Taxation rate, TR [128]	25%
Annual capacity degradation, Deg [129]	0.5%
Operation & Maintenance (O&M) [97]	5%

In these types of projects, the lifetime considered for the economic analysis is 20 years. By these means the results can be harmonised and include other technologies analysis like renewable generators, which technoeconomic analysis are also conformed in a similar time period. Nonetheless, it must be acknowledged that for electrochemical devices the technology lifetime does not only depend on time since its production, generally referred to as calendar life, but also the number of cycles. For vanadium redox flow batteries, a total number of 20 000 cycles through their lifetime is considered. The use profile of the system will then, modify the lifetime in a favourable way due to the low to no battery degradation when the system is off.

Moreover, as previously discussed, this lifetime limit often refers to the power system. If the power system is replaced, the energy tanks would still be used if proper regeneration and remixing techniques are carried out in the electrolytic tanks. If dismantling the system is the decided option at the end of the project, the electrolyte solutions could be sold highly increasing the residual value of the project lifetime. As it is considered a critical raw material for the EU, the prospective revenues are difficult to foresight given the wide temporal window.

Regarding more general financial parameters, it must be acknowledged that volatility and anomalies have been the norm in recent years. These parameters can affect the financial results, being recommended to adapt them for each case.

One of the most important parameters to determine is the Weighted Average Cost of Capital (WACC). This value can heavily depend on the investor considered and their financing method, as well as their risk profile towards an investment. A common approach is to consider the tables recommended by the national banks of the region scope. The implemented value in this case will be 3.25% considering the suggestion from the national Spanish bank [127]. This value has been considered constant through the project lifetime, but it could vary significantly through time, mainly affected by macro-economic factors such as inflation. Nonetheless, the value considered as the interest or money depreciation rate will be 10% to consider the revenues for the project developer.

The scope of this project focuses on Spain, considering a taxation rate of 25% according to the general type set by current legislation [128]. Depending on the type of industrial facility this percentage can vary down to 15%, as it is the case for recently established companies. The results expected when downing the taxation rate is to increase the profitability of the project as long as the revenues are positive.

Operation and maintenance costs are referred to the expenditures required to run the system. In this case, it is considered as 5% of the CAPEX [97]. Lower O&M values are reported in literature, such as 3% in the US [126], but the one referred to the European market is considered as more adequate for the project scope despite being less favourable for the economic results. This value includes costs associated to labour, electrolyte mixing, and regenerating process required to diminish the battery capacity fading [121].

Another cost to consider is the one associated to the energy used for charging the battery. It has been assumed that the battery performs a cycle per day, operating the same number of hours than the plant. In order to estimate the energy supplied to the battery during charge, the round-trip efficiency definition has been divided. Therefore, the energy demanded daily equals 20.53 MWh against the 15.4 MWh discharging capacity in the first year due to the safe margin oversize. Additionally, an annual capacity decay factor of 0.5% [129] has been considered for both the energy charged and discharged. The energy cost will be considered constant. Further optimisation of this cost can be reached by charging energy during low price hours, being possible to be zero or even a revenue depending on the spot electricity price.

Finally, the end-of-life cost occurring in the last year is implemented related to the disposal and residual value of the battery after the time considered. This value can be either positive or negative whether a cost or a revenue is implied. In literature this value is considered zero in most cases as a simplification hypothesis despite vanadium not losing the characteristics due to low to none aging effects. This value can be estimated to 70% of the CAPEX, meaning that only the remaining 30% would be necessary to refurbish the battery into a second life [121]. However, the uncertainty of the market in this time frame makes it difficult to estimate the future market and value of the technology. Both cases will be considered as a range.

Considering no end-of-life cost, a sensitivity analysis has been carried out considering different constant energy price during charge (Figure 42). A linear correlation is spotted, ranging from 30.761 to 117.109 M€ in the unitary energy price considered.

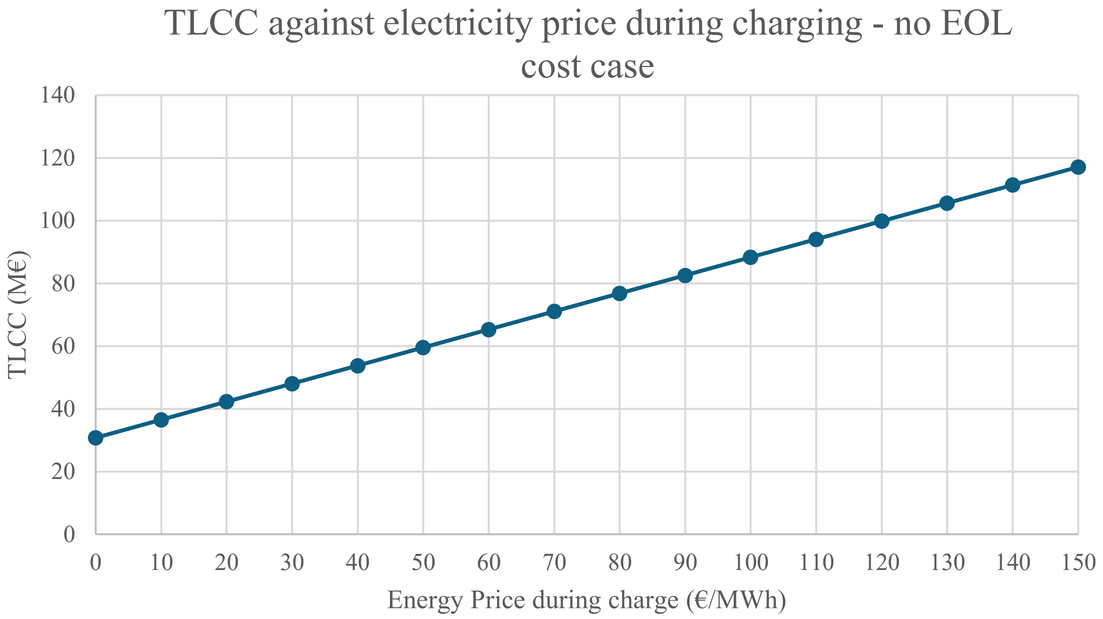


Figure 42. TLCC against mean electricity unitary price during charging considering no EOL cost.

As the EOL cost is computed once in the last year, the effect on the graph is a translation of the curve. The y-axis intersection is approximately 24.672 M€, significantly lower than the case where EOL has not been considered.

6.3. Levelized Cost of Storage

Levelized Cost of Storage can be conceived as an analogue financial indicator to Levelized Cost of Energy (LCOE). In this case, instead of dividing the TLCC by the total energy saved or generated during the project lifetime period [125], the energy stored is divided instead. This value can be seen as a way of measuring the different break-even points that favour the storage of energy. LCOS represents the price that justifies the investment and storage of energy. Therefore, if the overall electricity unitary price is higher than LCOS, storing energy at the specified electricity price during charge. The higher the electricity price, the higher the LCOS.

Considering the guidelines from the Spanish Institute of Energy Savings and Diversification (IDAE) [130], the LCOS should be calculated as the ratio between the TLCC previously defined without including the EOL component, and the energy discharged considering both depth of discharge and capacity degradation. Including the capacity fading factor of 0.5% per year [129], the energy stored annually ranges from 15.4 MWh in the first year until 13.94 MWh in the last year. The energy discharged during the project period under the simulation conditions is over 99.856 GWh, leading to a LCOS evolution considering different mean electricity prices during charge from 0.308 €/kWh to 1.173 €/kWh (Figure 43). The effect of the EOL cost is similar to the TLCC given the relation between both metrics, leading to a translation of the curve approximately equal to 0.061 €/kWh.

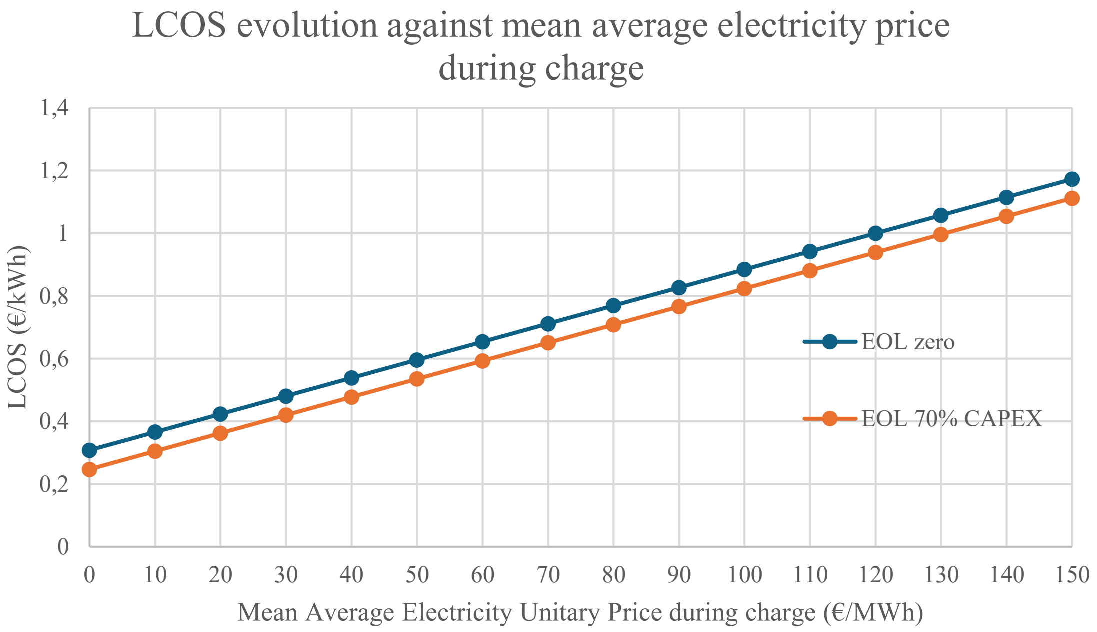


Figure 43. LCOS evolution against mean average electricity unitary cost during charge. EOL boundary conditions represented.

6.4. Sensitivity analysis

Input data should be procured directly from main sources such as specific manufacturing processes and specific batteries at operation sites [76]. Due to the difficulties to get this data, secondary or generic data will be used in this preliminary analysis when direct sources are not found. Data quality can have a significant impact on the results, and therefore further research and quality update is highlighted in the monitoring of KPIs. This is particularly important to data related to materials and electricity prices, where the volatility can severely affect the reliability and completeness of the data base used.

It is worth noting that most literature is expressed or considers non-European regions due to the higher development of the technology in those areas, such as the US. These values have been considered as a reference, but the actual price values considered in this study for costs estimation is based on European studies due to the area of interest.

6.4.1. Electricity market

The mean average price per month in the Spanish Peninsular electricity market from June 2023 until May 2024 that ranges from 32.3 to 112.4 €/MWh [131]. Apart from the energy spot price, the tariffs should be considered in the overall electricity price in order to achieve higher economic benefits. Moreover, ancillary services could be a source of benefits to explore. The sensitivity analysis is already embedded in the TLCC and LCOS studies where a linear dependency can be seen. This line delimits the regions where storing energy would be economically profitable if the electricity price is equal to the y-axis (Figure 44).

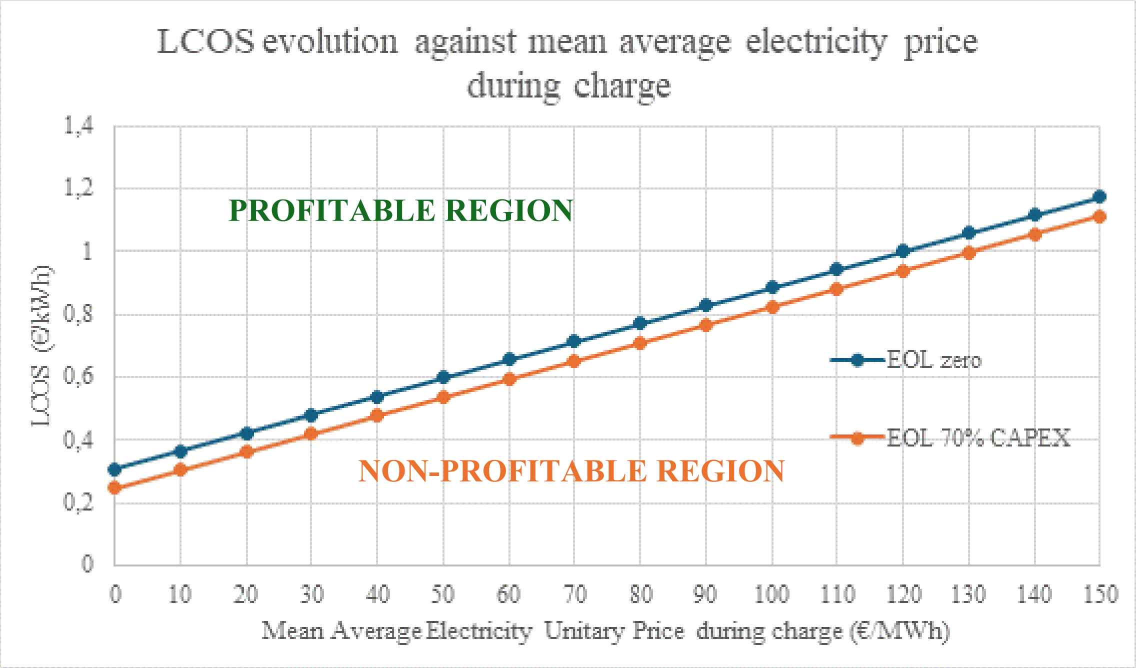


Figure 44. Profitability electricity price regions based on electricity charging price.

6.5.1. Vanadium price variation

Vanadium has been identified as the component that most impacted the CAPEX and, consequently, the financial metrics in the VRFB. The CAPEX and LCOS at a 10 €/MWh unitary electricity price during charge has been compared to the vanadium price variation within the ranges 4 and 60 €/kg, considering the market minimum and maximum prices over the last 25 years [106]. This analysis is especially useful as this parameter can heavily fluctuate and it can be monitored.

It is evident that the lower the vanadium cost, the lower the CAPEX (Figure 45) and LCOS (Figure 46). The evolution is linear for both parameters. However, the slopes of the zero EOL and 70% recovery differ as the later boundary conditions is affected by the CAPEX, being more sensible to this variation.

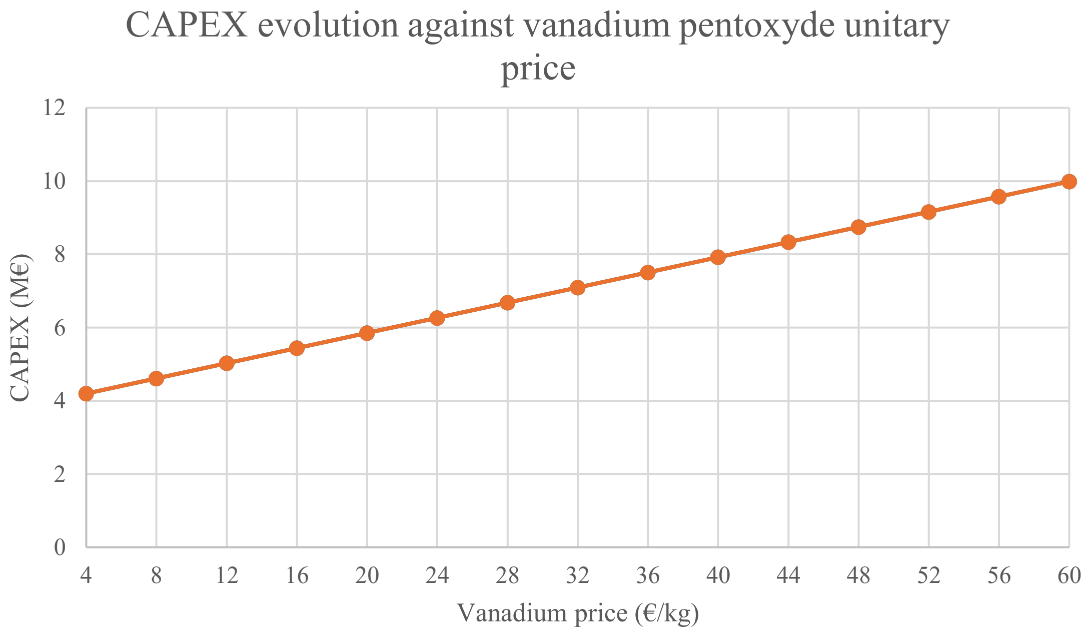


Figure 45. CAPEX Evolution against vanadium pentoxyde unitary price. Mean average unitary electricity Price during charging 10 €/MWh.

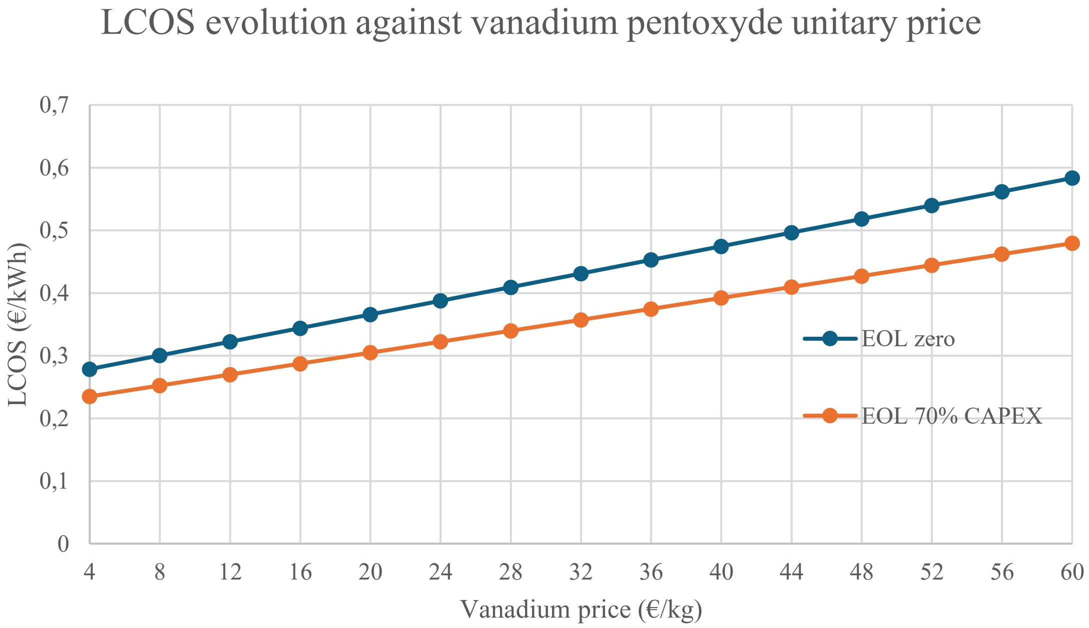


Figure 46. LCOS evolution against vanadium unitary price considering mean average unitary electricity price during charging 10€/MW.

Moreover, it must be acknowledged that these boundaries are subject to speculation, considering the uncertain evolution of vanadium price. The value could increase in the scenarios where vanadium becomes more critical or scarce, but the quantification of this effect is out of the scope of the project as it does not represent the client segment assessed.

6.6. Comparison between technologies

The indicators compared considering the client segment are CAPEX, LCOS, Efficiency and footprint (Table 16). As regards CAPEX, the thermal energy storage developed by the company is estimated to be over 1.5 M€, being a more competitive solution than the nearly 6 M€ required for VRFB. This aspect is one of the priorities of the costumer segment accessibility, which discards the VRFB as a competitor for industrial heat decarbonisation for 1-5 MW thermal demand. As it has been studied in the sensitivity analysis, this CAPEX is not competitive even when vanadium price is the lowest, so no economic threshold has been identified that can switch the prevalence of TES technology.

In terms of LCOS, the company product is over 0.06 €/kWh at an electricity price during charging equal to 30 €/MWh, considering both energy spot prices and TPA tariffs. The same value in the EOL 70%CAPEX recovery scenario is over 0,57 €/kWh, almost ten times higher. In this scenario, the technology is not as competitive as the company's one for the application considered.

The company's product estimates an efficiency of 92% conversion power to heat, being significantly higher than the best case of VRFB, estimated to be 85%. Efficiency for power-to-power applications, is benefited by the VRFB storing mechanism, being a more efficient storing technology. Considering this relation, VRFB are better for peak-shaving applications and industrial demands more intensive in electricity than heat.

Footprint is also one of the factors where VRFB is in disadvantage. In dense population areas where land is highly valued, this technology is not as beneficial for the power and energy range considered. Further analysis should be conducted depending on the location considered as this technoeconomic analysis is agnostic to land pricing. In this case, if the industrial user does not have the availability of an empty landfill, VRFB could not be implemented. Moreover, retrofitting of already existing plants seem less convenient due to the extensive land use. FTM applications seem to be a better suited application for VRFB as the requirements for land use are less restrictive.

Table 16. KPIs comparison between TES and VRFB for the case understudied.

	TES	VRFB
CAPEX	~1.5 M€	~5.85 M€
LCOS[1]	0.06 €/kWh	0.57 €/kWh
Round-trip efficiency	92%	65-85%
Materials Abundance	Abundant	Critical Raw Material
Footprint	14 m x 14 m	~ 10 times bigger

---

[1] At an average electricity price during charge equal to 30 €/MWh

7. Market analysis and future perspectives

In the latest years, important signals of change have been spotted in both geopolitics, social and planetary boundaries. This requires a change in the strategy followed by companies, industries and governments in order to better adapt to the uncertainty. The context can extremely impact the success of a technology and company, especially in the LDES sector where the list of technologies is long and the competitivity high.

The methodology followed in this chapter combines literature reviews including global and regional reports on LDES and VRFB future perspectives, but most importantly 1-on-1 interviews and experts' panels were a source of information to better understand the industry dynamics.

7.1. Market identification

LDES market is expected to grow significantly in the upcoming years, in order to enable renewable electricity implementation [61]. However, experts conclude that there is a wide range of technologies for a quite nascent market segment at the moment. The competition is big due to the high growth expectations, being identified as a promising asset to invest in [132]. Regarding redox flow batteries, the current market and competitor analysis has proved this statement right. Despite VRFB companies are relatively well-established in the market and big players are identified, new technologies are emerging fast for vanadium alternatives (Table 17).

Table 17. Redox Flow Battery Technology Manufacturers and companies. Own elaboration based on data from [67], [85], [122], [123], [129].

Technology	Manufacturer	Location	Maturity
All-Vanadium (VRFB)	CellCube	USA and Austria	High maturity, large product volumes manufactured, delivered and demonstrated in field i.e., 100MWh-1GWh [67].
	Invinity Energy Systems	UK	Commercial operation, modular designs available of over 250 kW per module [129].
	Rongke Power	China	Behind over 40 demonstration projects for flow battery. Behind current biggest VRFB commissioning of 100 MW/400 MWh in China [133].
	VRB Energy	USA	Commercial operation. Significant product volumes manufactured, delivered and demonstrated in the field (10MWh – 100MWh) [67].

	Sumitomo	China	Commercial operation. Pilot plants already running and modular designs available of over 250 kW per module [122], [123].
	STOREN	USA	Start-up under funding raise [134]
Zinc-Bromide ($ZnBr_2$ flow)	Redflow	Australia	Commercial operation. Significant product volumes manufactured, delivered and demonstrated in the field (10MWh – 100MWh) [67].
	Primus Power	USA	Product focuses on 25 kW modules of 5 hours storing capacity [135].
Zinc-Air	Abound (Previously Zinc8)	USA	Pre-commercial demonstration. Only small product volumes manufactured, delivered and demonstrated in the field [67].
	EOS	USA	12 years of testing and validation, now deployed globally .
Iron Flow (IRFB)	ESS Tech Inc.	USA	8. Commercial operation. Significant product volumes manufactured, delivered and demonstrated in the field (10MWh – 100MWh) [67].
Quinone	Quino Energy	USA	Start-up with strong participation in national and international forums [136]
	KEMIWATT	France	First organic Redox Battery prototype in 2016 and industrial demonstrator in 2017. Recently launched a partnership with MANN+HUMMEL to develop a new generation of RFB [137].

Nowadays, the frontrunner in LDES development, including redox flow batteries, is China. Other countries following closely and supporting LDES growth are the US, UK, Australia [74]. As for VRFB, China and USA are the main players accounting for the largest number of companies and capacity installed. In 2022, around 66% of both operation and announced/under construction VRFB capacity was installed in China, followed by USA (18%), Australia (8%) and Japan (6%) [103]. This technology is starting to gain traction in Europe, increasing the number of companies involved and projects. The European market seems to go under a time of change and investment on the technology has increased in the latest years as well as the number of pilot plants.

However, due to the high initial investment required this technology does not seem promising in Europe without any financing mechanism that favour the investment, but the lack of vanadium reserves in the EU does not play a favourable role towards its scale-up in Europe. The role of policies seems to be determinant in the success and competition of this technology, where the business models are still not mature despite the market prospects being ambitious.

Currently, most companies are start-ups with a strong academic background which makes the competition harder at a technology level. From a venture perspective, there is a wide list of LDES technologies, but with very similar performance KPIs. The main challenge is to convince customers on the added value and distinction of the LDES technology. The fit between use profile and the technology, as well as the communication is key for the success of the company. This part is especially important considering the strong research background of current market players, mostly start-ups [61]. Re-phrasing one of the interviewee's "The devil is on the details when it comes to LDES", where market timing and application-fit have been identified as one of the most important considerations for investors and users. This analysis confirms the importance of market fit and clients' identification, as well as competition analysis as an enabler for growth.

7.2. Incentives and barriers identification.

The long-term duration is one of the main added values that LDES bring, which have a favourable impact on the LCOS. However, this financial metric must not be the most decisive one when choosing the technology. On the other hand, the required initial investment might be a more relevant metric to choose between different technologies [66], as contrasted with experts on the field. Among others, the high cost and lack of viable material production facilities for rapidly producing the battery stack components is highlighted [102]. Nonetheless, the boost of hydrogen economy could be beneficial to overcome this barrier as the stacks components and assembling is similar to both technologies, leading to a cross-sectorial knowledge transfer.

Vanadium price volatility is identified as one of the main concerns for the understudied battery development. This fact can either be seen as a barrier or incentive to invest on it due to the regenerative aspects that can lead to a never-ending battery and/or vanadium recycling perpetuating the material time in the economy cycle. Recycling methods are already developed, easy to implement and the value incentive is more than justified given the scarcity of the material.

Low energy density reduces its competitiveness for BTM applications and areas where land cost is high. Nonetheless, this aspect might not be as decisive for FTM applications as the low capacity fading and regenerative capacities are highly valued, as well as competitive LCOS.

Its possibility to tailor energy and power ratio to the application seemed promising at the beginning, but there are some limitations for this incentive. Firstly, modularity can help reduce costs considering economies of scale. For this reason, 250 kW BTM applications can benefit from this advantage, but MW-order demands can heavily be affected by the footprint required. These modular designs consider varying energy capacities typically ranging from 2 to 12 hours, which can be seen as a compromise solution between economies of scale and energy and power sizing tailoring. In order to reduce the footprint for MW-scale applications, specific civil construction work that reduce the economies of scale benefits.

Lastly, current grid connection technical and regulatory frameworks are considered a barrier for the implementation of the technology. This barrier affects all type of energy storage and renewable energy projects, being LDES strongly affected. Among others, the EU market taxation system is considered not to favour the investment in LDES, despite the strategic benefits for the grid operators and society [25]. If ancillary services market gains importance in the upcoming years, the development of the technologies will be boosted, favoured by the adaptation of the revenue sharing mechanism to the system performance.

Table 18 summarizes the main barriers and incentives identified for VRFB deployment in the upcoming years.

Table 18. VRFB barriers and incentives summary. Own elaboration based on [64], [81], [85], [103], [104], [132].

Barriers	**Incentives**
High overall upfront capital expenditure	Longer asset life: No self-discharge and low-capacity fading
Vanadium is considered a CRM and experiences high price volatility	Recyclability: Never ending battery and vanadium regeneration
Difficulties regarding large-scale production and scale-up	Competitive operating cost (LCOS)
Low energy density leading to high footprints	Possibility to tailor energy and power ratio to the application
Low energy efficiency for an electrochemical system	Modular technology
Grid connection technical and regulatory challenges	Technological cross-transfer can faster the scale up
Electricity market does not favour LDES investment attraction.	Safety improvement when compared to LIBs

An additional incentive to consider is the role artificial intelligence could play in the development of vanadium redox flow batteries. The rise of Artificial Intelligence (AI) has been the most cross-sectorial disruptive effect of the past years. Its use can enable a reduction in cost and both the efficiency use of critical raw materials. Possible applications of AI improvements on the assessment and use of the technology range from KPIs and external factors forecast to optimisation of both EMS and BMS simultaneously [95].

The implementation of AI algorithms could be beneficial for the long-term assessment of the technology and optimisation of EMS. It could help improve the accuracy on future scenarios assessment for both revenues and costs flows, such as electricity prices and raw materials, as well as other technologies development. Caution needs to be taken in order to reduce biased algorithms that lead to misleading results by improving transparency on the model and good data training.

Additionally, AI-based models are rising interest in both modelling and optimisation of BMS operation strategies. Among the advantages, the enhancement on state estimation accuracy is highlighted, better adapting to diverse application scenarios [95].

Another advantage of implementing artificial intelligence is the linking between similar technologies and components. The learning curve of emerging technologies can significantly decrease considering the already existing data from commercial technologies. This will enable better assessed performance warranties, improving the market competitivity, but also predicting components degradation. An example would be membranes degradation, as the membranes used in VRFB are very similar to the ones used in PEM fuel cells. This factor is remarked to be crucial for some investors, as long-term is one of the main advantages of LDES and, therefore, one of the factors that may influence the final technology selection.

Last but not least, the implementation of AI-based optimisation algorithms could significantly improve the performance of digital twins. This use can bring value to any type of energy management tool, but this development is significant for non-lithium electrochemical energy storage, where digital twins development is one of the key research strategic actions [37].

7.3. Challenges assessment

As mentioned earlier, the multi-variable aspect on current economic frameworks includes a difficulty in the understanding of the context and challenges that a technology or product can face in the market. Awareness about market dynamics, but most importantly policy, environment and safety are gaining importance and complexity due to their own development. The potential vanadium redox flow batteries challenges highlighted include supply chain risks, cost competitivity, market, and financing risks, as well as policy and regulatory framework, environment and safety risks.

Supply chain risks are identified as the most severe factor for VRFB market success by World Bank [103]. The main concern is the resilience of the ecosystem due to the relatively nascent, despite several suppliers are already stablished along the value chain. Both manufacturing capability and raw materials accessibility are the main concerns regarding the value chain. The number of players with sufficient infrastructure and processing facilities is rather low and, as previously discussed, un-equally distributed around the globe.

Experts interviewed agree that the main challenges the LDES market face are the need for demonstration and cost competitiveness. Despite some pilot plans and small commercial plants are already running, getting customers early on is not an easy task. Vanadium redox flow batteries as the older technology seems to avoid this challenge, whereas companies and redox pairs with lower TRL (7-8) might face most significantly barriers related to manufacturing and supply chain before gaining early adoption in the market [67]. During Flow Battery Europe Webinar [138], over 35% of assistants agreed that the most important EU policy request for the development of the technology is supporting local manufacturing of flow batteries and the formation of the supply chain.

Market related risks are identified as the second most severe risk next to financing risks. The former is mostly referred to direct competition of alternative technologies in the same market segment, as it would be the case of the incipient post-lithium-ion electrochemical batteries. Whereas mechanical energy storage does not seem to be significant for the market niche studied given the low round-trip efficiency, other electrochemical batteries can be decisive on the market competition. The fast development of sodium-ion storage can be a prospective cost-competitive alternative that can encounter redox flow batteries deployment, as cost has been identified as the decisive criteria.

As mentioned before, the spread use of LIBs in EVs could enhance the economies of scale, as well as the development and enhancement of current lithium and post-lithium batteries such as sodium and potassium ion. These technologies launch could heavily influence the electrochemical stationary energy storage, leading to a tight competition. Currently, redox flow batteries outperform sodium-ion storage in terms of lifetime, although the abundance of sodium ion distribution in the coastal world surface could reduce the impact on cost and value chain problems when compared to VRFB. Sodium availability and geographical distribution could lead to a wider accessible market if the technology meets in terms of performance for stationary applications [62]. Moreover, energy storage hybridization defined as the complementary combination of different energy storage technologies in a system could suppose a challenge for redox flow batteries, as the effect on power and energy decoupling is reduced. In this sense, the prospective performance gain might not be enough to justify the higher investment required.

Financing risks are referred to the accessibility to low cost-financing opportunities in banks and financial institutions. The strong technical background required for assessing this type of projects may not favour the market entrance of small vendors. The risk associated to the market offtake due to the nascent state increases the inversion risk, where the bankruptcies do not distinguish between prominent players [103]. Market timing is the final parameter that financial institutions and investors consider in order to invest or not in a technology. As for now, the cost and establishment of the technology does not look promising towards its deployment.

Despite the cost competitivity in the long term, the high upfront cost is one of the main barriers that the technology faces as previously discussed. Cost economics and pricing risks are highlighted as the fourth most severe factor [103]. Among others, leasing models have been suggested in order to diminish the initial investment required for the users and incentivise the technology deployment. Business models are seen as a strategic way to convince clients of the technology benefits, especially due to the reduced number of proven commercial examples. This strategy has been successful to develop efficiency and energy savings projects, as the project benefits might be difficult to quantify and understand.

Additionally, miscellaneous risks including policy and regulatory framework, economies of scale, and health, environment and safety risks are considered. Despite being identified as the least severe risks by the World Bank [103], its contemplation is crucial and can significantly affect the technology acceptance. As regards policy and regulatory framework there are no specific roadmap or programme aimed for flow batteries exclusively, as it is the case with other technologies such as hydrogen. Nonetheless, it is worth mentioning that some change can be spotted, and more associations are emerging as Flow Batteries Europe, which mission is to help shaping the legal framework at the EU level and contribute the EU decision-making process [138].

In the case of health, environment and safety risks an improvement when compared to LIBs can be achieved. However, vanadium redox flow batteries seem to be more detrimental for human health and pollution than others redox flow batteries. The main reason behind this discrepancy is associated with vanadium pentoxide electrolyte production [103]. Alternative chemistries in redox flow batteries could be beneficial in this sense, covering the market if performance characteristics are enhanced.

As any product, redox flow batteries market is heavily influenced by economic, market trends and geopolitics. Both industrial value chain deployment and vanadium price volatility are heavily affected by geopolitical concerns and can severely affect the evolution and adaption of redox flow batteries. Raw materials diversification and development of other redox flow couples is one strategic line to follow. On the other hand, policies should reinforce regional strategic value chains to avoid disruptions in supply.

7.4. Key Performance Indicators

KPIs importance can heavily depend on the application considered. As an example, round trip efficiency plays a major role in short-duration energy storage, whereas self-discharge is a more relevant parameter in seasonal storage. On the use case studied, the most relevant parameters identified are vanadium price, LCOS, CAPEX, round-trip efficiency and energy density measured indirectly by the expected footprint. These parameters were compared in the techno-economic assessment chapter with the company's current product (Table 16). Additionally, materials abundance has been considered as an important parameter for future identification as it could heavily influence the decision-making process. Although this aspect is embedded in the vanadium price, the relation with the economic feasibility is project specific. From the point of view of a developer, the scalability is a major concern in a growth market, being this the reason of emphasis.

In the scenario considered, VRFB are not considered a competitive threat nor a viable product in the company's market niche. However, KPIs monitoring is recommended in order to identify its future viability.

Vanadium price is the most critical KPI to consider, as it is the one affecting the CAPEX the most, considered the most critical aspect damaging the technology attractiveness. In the sensibility analysis no economic threshold at which the vanadium price could change the decision towards VRFB was found. A solution discussed by experts in order to reduce this negative effect is the development of business models such as leasing VRFB as a service. Others indicate that a global association that could overview and bring stability to the price, as it is the case for nuclear fuel, could significantly improve these issues.

In any case, only a major overall cost reduction could be enough to turn the tables towards redox flow batteries. A solution would be new chemistries, as they are claimed to improve VRFB in aspects such as CAPEX, energy density, and environmental footprint. Other chemistries TRL has been additionally identified as an important KPI for future competitor identification. Major breakthroughs that surpass the currently set KPIs as well as delivering the same warranties in terms of durability should be considered. The chemistries under the scope are all-iron RFBs, Zinc-Bromine RFBs and organic-based considering the state-of-the-art.

7.5. Potential markets

There is no fit-for-all solution in economy decarbonisation and a combination of clean technologies should be considered in order to achieve the so-wanted Net Zero Scenarios. Choosing the most suitable technology for the application is, therefore, not only a money-driven decision, but also a compromise with humanity and the environment. Allocating the limited resources properly without compromising economic development is one of the key challenges that humanity faces nowadays. Redox Flow Batteries, as LDES technology will play a crucial role in achieving these goals. Despite the cost, the long-term and easy recyclability makes it a good investment for long-term applications and investment.

Market timing and readiness are key in the success of a technology. Markets where electricity prices and the regulatory framework are favourable should be considered as early adopters. In the US, California is seen as one of the prospective markets due to this reason [61]. In Europe, the similarities in terms of energy mix between California and Spain in these aspects, is a sign of the adequacy of the scope considered. In the EU, prospective early adopters are Germany, Portugal, and Italy given the high VRE share trends, especially solar PV [139], [140].

Considering that the main benefits of the technology are associated with the unlimited regeneration of the battery, low self-discharge and LCOS, the best market niche seems to be FTM applications, such as peak shaving. These applications are aimed for a long duration and extendable, if possible, in order to maximise the benefits once a connection point is obtained. Grid connection points are usually the bottle neck for these projects, which location can influence in the footprint importance as a KPI. Nonetheless, this aspect is less restrictive for FTM than BTM applications.

The high initial investment difficult the spread of the technology despite the competitive LCOS. Policy and regulatory frameworks may highly influence its deployment by either changing market pricing mechanisms or other incentives towards LDES [25], which seems justified by the consequent societal gains that the technology could bring.

8. Conclusion

LDES is a prospective growth market that is raising attention and could have benefits for both investors and clients in the short to medium term. Given the relative nascent market and strong research background of actors, understanding industry dynamics, competitors value proposition and technology development at the set pace are key to success. Considering redox flow batteries development in recent years, an analysis on the technology and techno-economic analysis based on a relevant industrial case in the company's market niche was carried out.

Among the different redox flow batteries, all-vanadium was considered the reference technology due to its high durability and TRL. However, it was not identified as a competitor in the same market niche as the company assessed. Based on the initial investment, operational cost and efficiency redox flow batteries are not economic attractive for the application considered when compared to thermal energy storage. Therefore, it can be concluded that the technology, as of now, is not a threat to the company's market niche nor a prospective product.

Whereas both markets can be interconnected, TES is predominantly the most suitable solution for power-to-heat technologies. Nonetheless, the power and energy decouple seemed to be a good option for industrial users that present high power demand profiles, as it has been identified as the most suitable industrial demand for the technology. However, this advantage has not been enough to overcome the efficiency of heat-to-heat technologies. The main KPIs to consider for future tracking of the technology development are:

- CAPEX.
- LCOS
- Efficiency
- Energy density.
- TRL in new chemistries including durability.

CAPEX, efficiency, and energy density have been identified as the main indicators for the market niche. Regarding CAPEX, vanadium has been spotted as the most significant component corresponding to over 29.45% of the CAPEX, followed by the stack cost and assembly. Vanadium price impact has been categorized as significant for the battery CAPEX and LCOS, but still no cost reduction is enough to compete with the company's product. Due to the expected reduction and possible cross-sectorial development, the stack and assembly costs are expected to decrease. However, it is not expected an abrupt cost decline that supposes a competition in the medium-term.

Regarding efficiency, the main loss is associated with the pumping system. Frequent charging and discharging can severely affect the roundtrip efficiency and be detrimental to the overall system performance. In cases where short- and long-term storage is required, hybridization cases should be considered. The user energy and power profile are key in order to provide a resource-efficient and, consequently, cost-competitive solution. Further research on the battery dynamics and optimisation of the overall energy system are key areas of development that could improve efficiency and consequently reduce costs.

The development of other redox flow batteries chemistries is measured by the TRL, although durability should be included as it was the former criteria of dismissal. The expected lower cost of systems such as all-iron flow batteries and the environmental improvement could be the next relevant battery system to study. Other technologies such as Zinc-bromine RFB could improve energy density and CAPEX if the durability limit is improved. Other low-TRL technologies could significantly scale including organic-based RFB, being also an opportunity to improve energy density. Research and development play a major role in the future of redox flow batteries, as well as materials diversification.

Whereas vanadium redox flow batteries do not solve the dependence on critical raw materials, diversification and the unlimited recyclability could be a good reason to invest on the technology. Nonetheless, the high up-front cost and the added value rather fall in the Government and regional interests, than free market competition in BTM applications. For this reason, the user case studied is not the most relevant for the technology but stays a promising large-scale grid energy storage solution instead. Considering the high recyclability of vanadium leading to a never-ending battery, this longer asset life is better suited with other markets such as FTM applications. Grid peak shaving has been considered as a better market fir for early adopters.

Spain seems to be the perfect European country to deploy the technology given the high variable renewable energy shares potentials and ambitions, as well as the regulatory framework. These characteristics makes them the best market entry in the EU for LDES in general, as it is highlighted in literature. Other prospective EU countries to consider are Germany, Italy and Portugal, considering the expected high share of VRE.

9. References

[1] IEA, “World Energy Outlook 2023,” Paris, Oct. 2023. Accessed: Apr. 28, 2024. [Online]. Available: https://www.iea.org/reports/world-energy-outlook-2023

[2] IPCC, “Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change,” 2021. doi: 10.1017/9781009157896.001.

[3] IPCC, “Climate Change 2023: Synthesis Report,” Geneva, Switzerland, 2023. Accessed: Feb. 17, 2024. [Online]. Available: https://www.ipcc.ch/report/ar6/syr/downloads/report/IPCC_AR6_SYR_LongerReport.pdf

[4] H. Riebeek, “The Carbon Cycle,” NASA Earth Observatory. Accessed: Apr. 27, 2024. [Online]. Available: https://earthobservatory.nasa.gov/features/CarbonCycle

[5] IPCC, “Climate Change 2022: Impacts, Adaptation and Vulnerability,” 2022. Accessed: Jan. 07, 2023. [Online]. Available: https://report.ipcc.ch/ar6/wg2/IPCC_AR6_WGII_FullReport.pdf

[6] C. Pettengell, “Adressing the Triple Emergency: Poverty, Climate Change, and Environmental Degradation,” Apr. 2020. Accessed: Apr. 28, 2024. [Online]. Available: https://cdn.wcs.org/2020/06/23/15fkue6vvv_bond_adressing_the_triple_emergency.pdf?_ga=2.108638916.713216037.1713968635-605111319.1713968635&_gl=1*cne878*_ga*NjA1MTExMzE5LjE3MTM5Njg2MzU.*_ga_BTX9HXMYSX*MTcxMzk2ODYzNS4xLjEuMTcxMzk2OTEzNS42MC4wLjA

[7] United Nations, “The 17 Goals,” Department of Economic and Social Affairs. Sustainable Development. Accessed: Apr. 28, 2024. [Online]. Available: https://sdgs.un.org/goals#icons

[8] European Council. Council of the European Union, “Fit for 55,” European Green Deal. Accessed: Apr. 04, 2023. [Online]. Available: https://www.consilium.europa.eu/en/policies/green-deal/fit-for-55-the-eu-plan-for-a-green-transition/

[9] Eurostat, “Shedding light on energy in Europe - 2024 Edition,” 2024. doi: 10.2785/88627.

[10] Eurostat, “Energy imports dependency,” Data Browser. Accessed: Apr. 28, 2024. [Online]. Available: https://ec.europa.eu/eurostat/databrowser/view/nrg_ind_id/default/table?lang=en

[11] European Commission, “REPowerEU Plan,” Brussels, May 2022. Accessed: Dec. 30, 2022. [Online]. Available: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52022DC0230

[12] European Commission, “The Net-Zero Industry Act: Accelerating the transition to climate neutrality,” Internal Market, Industry, Entrepreneurship and SMEs. Accessed: Apr. 28, 2024. [Online]. Available: https://single-market-economy.ec.europa.eu/industry/sustainability/net-zero-industry-act_en

[13] European Commission, “Critical Raw MAterials: ensuring secure and sustainable supply chains for EU’s green and digital future,” European Commission Press Release. Accessed: Apr. 28, 2024. [Online]. Available: https://ec.europa.eu/commission/presscorner/detail/en/ip_23_1661

[14] U.S. Department of the Treasury, “Inflation Reduction Act,” Policy Issues. Accessed: Apr. 28, 2024. [Online]. Available: https://home.treasury.gov/policy-issues/inflation-reduction-act#:~:text=On%20August%2016%2C%202022%2C%20President,made%20in%20the%20nation’s%20history.

[15] European Commission, “Carbon leakage,” European Commission. Energy, Climate Change, Environment. Accessed: Apr. 28, 2024. [Online]. Available: https://climate.ec.europa.eu/eu-action/eu-emissions-trading-system-eu-ets/free-allocation/carbon-leakage_en

[16] IEA, “Greenhouse Gas Emissions from Energy Data Explorer,” Energy Data Explorer. Accessed: Apr. 28, 2024. [Online]. Available: https://www.iea.org/data-and-statistics/data-tools/greenhouse-gas-emissions-from-energy-data-explorer

[17] IEA, “Europe. Emissions,” IEA Countries & Regions. Accessed: Apr. 28, 2024. [Online]. Available: https://www.iea.org/regions/europe/emissions

[18] T. Gerres and P. Linares, “Perspectives on the industrial transformation towards a green economy,” Jan. 2024. Accessed: Feb. 17, 2024. [Online]. Available: https://www.fundacionnaturgy.org/publicacion/perspectivas-para-la-transformacion-industrial-hacia-una-economia-verde/

[19] S. Read and I. Shine, “You’ve probably heard of Scope 1, 2 and 3 emissions, but what are Scope 4 emissions?,” World Economic Forum. Accessed: Apr. 28, 2024. [Online]. Available: https://www.weforum.org/agenda/2022/09/scope-4-emissions-climate-greenhouse-business/

[20] Greenhouse Gas Protocol, “Product Life Cycle Accounting and Reporting Standard,” Sep. 2011. Accessed: Apr. 28, 2024. [Online]. Available: https://ghgprotocol.org/sites/default/files/standards/Product-Life-Cycle-Accounting-Reporting-Standard_041613.pdf

[21] IEA, “Ammonia Technology Roadmap,” Paris, Oct. 2021. Accessed: Apr. 28, 2024. [Online]. Available: https://iea.blob.core.windows.net/assets/6ee41bb9-8e81-4b64-8701-2acc064ff6e4/AmmoniaTechnologyRoadmap.pdf

[22] H. Proff, B. Lorentz, C. Gutglück, and C. Cruceru-Weisbrod, “Automotive: Pathways to decarbonization,” 2023. Accessed: Apr. 28, 2024. [Online]. Available: https://www2.deloitte.com/content/dam/Deloitte/es/Documents/manufacturing/Deloitte-es-manufacturing-descarbonizacion-sector-automocion.pdf

[23] IEA, “Trackling Clean Energy Progress 2023,” Paris, Jul. 2023. Accessed: Apr. 29, 2024. [Online]. Available: https://www.iea.org/reports/tracking-clean-energy-progress-2023#overview

[24] IEA, “Net Zero by 2050,” Paris, 2021. Accessed: Mar. 19, 2024. [Online]. Available: https://www.iea.org/reports/net-zero-by-2050

[25] SYSTEMIQ, “Catalysing the Global Opportunity for Electrothermal Energy Storage,” Feb. 2024.

[26] Beyond Zero Emissions, “Zero Carbon Industry Plan: Electrifying Industry,” 2018. [Online]. Available: http://bze.org.au

[27] IRENA, “Renewable Power Generation Costs in 2022,” Abu Dhabi, Aug. 2023.

[28] IEA, “Renewables 2023,” Paris, Jan. 2024. Accessed: Jan. 22, 2024. [Online]. Available: https://www.iea.org/reports/renewables-2023?utm_campaign=IEA+newsletters&utm_medium=Email&utm_source=SendGrid

[29] European Commission, “Commission sets out actions to accelerate the roll-out of electricty grids,” European Commission Press Corner. Accessed: May 01, 2024. [Online]. Available: https://ec.europa.eu/commission/presscorner/detail/en/ip_23_6044

[30] IRENA, “Electricity storage and renewables: Costs and markets to 2030,” Oct. 2017.

[31] EASE, “Energy Storage Targets 2030 and 2050. Ensuring Europe’s Energy Security in a Renewable Energy System,” Brussels, Jun. 2022.

[32] European Commission, “Recommendations on energy storage,” Energy, Climate Change and Environment. Accessed: May 05, 2024. [Online]. Available: https://energy.ec.europa.eu/topics/research-and-technology/energy-storage/recommendations-energy-storage_en

[33] T. M. Letcher, “Storing Energy,” 2022.

[34] IEA, “Introduction to System Integration of Renewables,” Paris, 2020. Accessed: May 02, 2024. [Online]. Available: https://www.iea.org/reports/introduction-to-system-integration-of-renewables

[35] IEA, “Energy Technology Perspectives 2023,” Paris, 2023. Accessed: Feb. 27, 2024. [Online]. Available: https://www.iea.org/reports/energy-technology-perspectives-2023

[36] IEA, “Batteries and Secure Energy Transitions,” Apr. 2024.

[37] Batteries European Partnership (BATT4EU), “Strategic Research & Innovation Agenda,” Feb. 2024. Accessed: Apr. 02, 2024. [Online]. Available: https://bepassociation.eu/our-work/sria/

[38] M. Linder, J. Noffsinger, R. Riesebieter, K. Somers, H. Tai, and G. van Gendt, “Net-zero heat: Long-duration energy storage to accelerate energy system decarbonization,” Nov. 2022. Accessed: May 12, 2024. [Online]. Available: https://www.mckinsey.com/capabilities/sustainability/our-insights/net-zero-heat-long-duration-energy-storage-to-accelerate-energy-system-decarbonization#/

[39] Build To Zero S.L., “Build To Zero Company.” Accessed: May 05, 2024. [Online]. Available: https://buildtozero.es/

[40] LDES Council, “Driving to Net Zero Industry Through Long Duration Energy Storage,” Nov. 2023. Accessed: May 05, 2024. [Online]. Available: https://www.ldescouncil.com/assets/pdf/LDES_Net_Zero_Industry_Report.pdf

[41] I. Ito Iwakiri, T. Antunes, H. Almeida, J. Sousa, R. Figueira, and A. Mendes, “Redox Flow Batteries: Materials, Design and Prospects,” *Energies (Basel)*, vol. 14, Sep. 2021, doi: 10.3390/en14185643.

[42] IRENA, “Renewable Power Generation Costs in 2021,” Jul. 2022.

[43] SolarPACES, “CSP Projects Around the World,” Solar Power & Chemical Energy Systems.

[44] IEA-PVPS, “2024 Snapshot of Global PV Markets,” Apr. 2024. Accessed: May 02, 2024. [Online]. Available: https://iea-pvps.org/wp-content/uploads/2024/04/Snapshot-of-Global-PV-Markets_20241.pdf

[45] Red Eléctrica, “REData Potencia Instalada,” REData Generación. Accessed: May 02, 2024. [Online]. Available: https://www.ree.es/es/datos/generacion/potencia-instalada

[46] Red Eléctrica, “Informe del Sistema Eléctrico 2023,” Mar. 2024. Accessed: May 02, 2024. [Online]. Available: https://www.sistemaelectrico-ree.es/sites/default/files/2024-03/ISE_2023.pdf

[47] “How the Iberian Exception Operates,” 2023.

[48] red eléctrica, “Informe del Sistema Eléctrico 2022,” Mar. 2023. Accessed: May 07, 2023. [Online]. Available: https://www.sistemaelectrico-ree.es/sites/default/files/2023-03/ISE_2022.pdf

[49] Red Eléctrica, “Intercambios 2023,” Informes del Sistema. Accessed: May 02, 2024. [Online]. Available: https://www.sistemaelectrico-ree.es/informe-del-sistema-electrico/intercambios/francia

[50] Statista, “Number of operational and planned LNG terminals in Europe as of January 2024, by country,” Chemicals & Resources. Accessed: May 02, 2024. [Online]. Available: https://www.statista.com/statistics/326008/lng-import-terminals-by-country-europe/

[51] Ministerio para la Transición Ecológica y el Reto Demográfico, "Informe de Inventario Nacional Gases de Efecto Invernadero," Mar. 2023. Accessed: May 04, 2024. [Online]. Available: https://www.miteco.gob.es/content/dam/miteco/es/calidad-y-evaluacion-ambiental/temas/sistema-espanol-de-inventario-sei-/es_nir_edicion2023_tcm30-560374.pdf

[52] Ministerio para la Transición Ecológica y el Reto Demográfico, "Plan Nacional Integrado de Energía y Clima (PNIEC) 2021-2030," Madrid, Jan. 2020. Accessed: Feb. 27, 2024. [Online]. Available: https://www.miteco.gob.es/content/dam/miteco/es/ministerio/planes-estrategias/plan-nacional-integrado-energia-clima/plannacionalintegradodeenergiayclima2021-2030_tcm30-546623.pdf

[53] Ministerio para la Transición Ecológica y el Reto Demográfico (MITECO), "Plan Nacional de Adaptación al Cambio Climático," Madrid, 2020. Accessed: Nov. 18, 2023. [Online]. Available: https://www.miteco.gob.es/content/dam/miteco/es/cambio-climatico/temas/impactos-vulnerabilidad-y-adaptacion/pnacc-2021-2030_tcm30-512163.pdf

[54] Gobierno de España, "Proyectos estratégicos para la recuperación y transformación económica (PERTE)." Accessed: May 01, 2024. [Online]. Available: https://planderecuperacion.gob.es/como-acceder-a-los-fondos/pertes#descarbonizacion

[55] J. S. Iversen, "Futures Thinking Methodologies and Options for Education," 2006, pp. 107–120. doi: 10.1787/9789264023642-8-en.

[56] OpenModellica, "Modelica Courses." Accessed: Apr. 04, 2024. [Online]. Available: https://openmodelica.org/useresresources/modelica-courses/

[57] TRNSYS, "TRNSYS: Transient System Simulation Tool." Accessed: Apr. 04, 2024. [Online]. Available: https://www.trnsys.com/index.html

[58] COMSOL, "COMSOL Learning Center." Accessed: Apr. 04, 2024. [Online]. Available: https://www.comsol.com/support/learning-center

[59] COMSOL Software License Agreement 6.1, *Vanadium Redox Flow Battery*. Accessed: Apr. 22, 2024. [Online]. Available: https://www.comsol.com/model/download/1047941/models.battery.v_flow_battery.pdf

[60] Endesa, "Are we ready to face a prolonged drought in Spain?," The e face. Accessed: May 11, 2024. [Online]. Available: https://www.endesa.com/en/the-e-face/climate-change/measures-alleviate-drought-effects

[61] U.S. Department of Energy, "Pathways to Commercial Liftoff: Long Duration Energy Storage," Mar. 2023. Accessed: May 18, 2024. [Online]. Available:

https://liftoff.energy.gov/wp-content/uploads/2023/03/20230320-Liftoff-LDES-vPUB.pdf

[62] Batteries Europe. European Technology and Innovation Platform, “Roadmap on Stationary Applications for Batteries.” Accessed: Apr. 02, 2023. [Online]. Available: https://energy.ec.europa.eu/system/files/2022-01/vol-6-009.pdf

[63] I. Chernyakhovskiy, T. Bowen, C. Gokhale-Welch, and O. Zinaman, “USAID Energy Storage Decision Guide for Policymakers,” Jul. 2021. Accessed: May 05, 2024. [Online]. Available: https://www.nrel.gov/docs/fy21osti/78815.pdf

[64] A. Clemente and R. Costa-Castelló, “Redox Flow Batteries: A Literature Review Oriented to Automatic Control,” *Energies (Basel)*, vol. 13, no. 17, 2020, doi: 10.3390/en13174514.

[65] IRENA, “Geopolitics of the Energy Transformation: The Hydrogen Factor,” 2022. Accessed: Dec. 30, 2022. [Online]. Available: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2022/Jan/IRENA_Geopolitics_Hydrogen_2022.pdf

[66] K. Sherwood, K. Rodby, S. Abdelrazek, C. Galán, J. O’brien, and P. Saha, “Webinar- Unlocking Financing for Long-Duration Energy Storage Projects in the US: Strategies for Success,” RENMAD Storage USA LDES, May 16, 2024.

[67] Ara Ake, “Stationary Battery Energy Storage Systems Analysis,” Mar. 2023.

[68] IRENA, “Innovation Outlook: Thermal Energy Storage,” Abu Dhabi, 2020.

[69] EASE, “Thermal Energy Storage,” Brussels, Sep. 2023.

[70] IRENA, “Innovation Landscape for Smart Electrification. Decarbonising End-Use Sectors with Renewable Power,” Abu Dhabi, 2023.

[71] MIT Energy Initiative, “The Future of Energy Storage,” 2022.

[72] D. Linen and T. B. Reddy, *Handbook of Batteries*, 3rd ed. McGraw-Hill, 1995.

[73] BloombergNEF, “Lithium-Ion Battery Pack Prices Hit Record Low of $139/kWh,” BloombergNEF. Accessed: May 18, 2024. [Online]. Available: https://about.bnef.com/blog/lithium-ion-battery-pack-prices-hit-record-low-of-139-kwh/

[74] Y. Sekine, “Energy Storage: 10 Things to Watch in 2024,” BloomberNEF. Accessed: May 18, 2024. [Online]. Available: https://about.bnef.com/blog/energy-storage-10-things-to-watch-in-2024/

[75] C. Schubert *et al.*, “Hybrid Energy Storage Systems Based on Redox-Flow Batteries: Recent Developments, Challenges, and Future Perspectives,” *Batteries*, vol. 9, Mar. 2023, doi: https://doi.org/10.3390/batteries9040211.

[76] S. Passerini, L. Brelli, M. Baumann, J. Peters, and M. Weil, *Emerging Battery Technologies to Boost the Clean Energy Transition*, 1st ed. Springer Cham, 2024. doi: https://doi.org/10.1007/978-3-031-48359-2.

[77] E. Sánchez-Díez *et al.*, "Redox flow batteries: Status and perspective towards sustainable stationary energy storage," *J Power Sources*, vol. 481, p. 228804, Jan. 2021, doi: 10.1016/J.JPOWSOUR.2020.228804.

[78] J. Mitali, S. Dhinakaran, and A. A. Mohamad, "Energy storage systems: a review," *Energy Storage and Saving*, vol. 1, no. 3, pp. 166–216, Sep. 2022, doi: 10.1016/J.ENSS.2022.07.002.

[79] L. Liyu, K. Soowhan, X. Gordon, W. Wei, and Y. Z. Gary, "Advanced Redox Flow Batteries for Stationary Electrical Energy Storage," Richland, Washington, Feb. 2012.

[80] M. L. Perry, K. E. Rodby, and F. R. Brushett, "Untapped Potential: The Need and Opportunity for High-Voltage Aqueous Redox Flow Batteries," *ACS Energy Lett*, vol. 7, no. 2, pp. 659–667, 2022, doi: 10.1021/acsenergylett.1c02225.

[81] A. Trovò, "Industrializing Vanadium Redox Flow Battery," Università degli Studi di Padova, Padova, 2019. Accessed: Jun. 16, 2024. [Online]. Available: https://www.research.unipd.it/handle/11577/3422708

[82] T. Puleston, A. Clemente, R. Costa-Castelló, and M. Serra, "Modelling and Estimation of Vanadium Redox Flow Batteries: A Review," *Batteries*, vol. 8, no. 121, Sep. 2022, doi: https://doi.org/10.3390/batteries8090121.

[83] L. J. Small, C. H. Fujimoto, H. D. Pratt III, and T. M. Anderson, "Redox Flow Batteries," in *U.S. DOE Energy Storage Handbook*, Sandia National Laboratories, 2020.

[84] H. Zhang and C. Sun, "Cost-effective iron-based aqueous redox flow batteries for large-scale energy storage application: A review," *J Power Sources*, vol. 493, p. 229445, May 2021, doi: 10.1016/J.JPOWSOUR.2020.229445.

[85] I. Careaga, "REDOX FLOW BATTERIES: POTENTIAL, ALTERNATIVES AND CHALLENGES," CIC EnergiGUNE Blog. Accessed: May 18, 2024. [Online]. Available: https://cicenergigune.com/en/blog/redox-flow-batteries-potential-alternatives-challenges

[86] G. P. Rajarathnam, "The Zinc/Bromine Flow Battery: Fundamentals and Novel Materials for Technology Advancement," The University of Sydney, Sydney, 2016. Accessed: Jun. 01, 2024. [Online]. Available: https://ses.library.usyd.edu.au/handle/2123/16394

[87] X. Ke, J. M. Prahl, J. I. D. Alexander, J. S. Wainright, T. A. Zawodzinski, and R. F. Savinell, "Rechargeable redox flow batteries: flow fields, stacks and design considerations," *Chem Soc Rev*, vol. 47, no. 23, pp. 8721–8743, 2018, doi: 10.1039/C8CS00072G.

[88] K. Knehr, E. Agar, C. Dennison, A. Kalidindi, and E. Kumbur, "A Transient Vanadium Flow Battery Model Incorporating Vanadium Crossover and Water

Transport through the Membrane," *J Electrochem Soc*, vol. 159, pp. A1446–A1459, Aug. 2012, doi: 10.1149/2.017209jes.

[89] California Energy Comission, "Life Cycle Assessment of Environmental and Human Health Impacts of Flow Battery Energy Storage Production and Use," Irvine, Dec. 2021.

[90] A. A. Shah, M. J. Watt-Smith, and F. C. Walsh, "A dynamic performance model for redox-flow batteries involving soluble species," *Electrochim Acta*, vol. 53, no. 27, pp. 8087–8100, Nov. 2008, doi: 10.1016/J.ELECTACTA.2008.05.067.

[91] D. Bordignon, "Modelling of All Vanadium Redox Flow Batteries with COMSOL Multiphysics," Padova, 2024.

[92] T. M. Rodrigues Lagarteira, "Electrochemical technologies for renewable energy storage," Universidade do Porto, Porto, 2023. Accessed: May 30, 2024. [Online]. Available: https://repositorio-aberto.up.pt/handle/10216/157090

[93] N. M. Azevedo Dias Lima Delgado, "Modelling and design optimization of all-vanadium redox flow batteries," Universidade do Porto, Porto, 2023. Accessed: May 30, 2024. [Online]. Available: https://repositorio-aberto.up.pt/handle/10216/141722

[94] M. Jafari, K. Rodby, J. L. Barton, F. Brushett, and A. Botterud, "Improved Energy Arbitrage Optimization with Detailed Flow Battery Characterization," in *2019 IEEE Power & Energy Society General Meeting (PESGM)*, 2019, pp. 1–5. doi: 10.1109/PESGM40551.2019.8974070.

[95] H. Wang, S. A. Pourmousavi, W. L. Soong, X. Zhang, and N. Ertugrul, "Battery and energy management system for vanadium redox flow battery: A critical review and recommendations," *J Energy Storage*, vol. 58, p. 106384, Feb. 2023, doi: 10.1016/J.EST.2022.106384.

[96] A. Karrech, K. Regenauer-Lieb, and F. Abbassi, "Vanadium flow batteries at variable flow rates," *J Energy Storage*, vol. 45, p. 103623, Jan. 2022, doi: 10.1016/J.EST.2021.103623.

[97] C. Minke, U. Kunz, and T. Turek, "Techno-economic assessment of novel vanadium redox flow batteries with large-area cells," *J Power Sources*, vol. 361, pp. 105–114, Sep. 2017, doi: 10.1016/J.JPOWSOUR.2017.06.066.

[98] P. Á. Prieto-Díaz, A. A. Maurice, and M. Vera, "Measuring density and viscosity of vanadium electrolytes: An exhaustive database with multivariate polynomial fits," Mar. 2024. doi: doi:10.26434/chemrxiv-2024-dnmq7.

[99] C. A. Pino-Muñoz, "MATHEMATICAL MODELLING OF VANADIUM-BASED REDOX FLOW BATTERIES," Imperial College London, London, 2020.

[100] E. Commission, D.-G. for Energy, S. Fawkes, P. Sweatman, L. Bedford, and M. Hafner, *Launch and facilitate the implementation of new EEFIG Working Group*

“Applying the Energy Efficiency First principle in sustainable finance” – Final report. Publications Office of the European Union, 2023. doi: doi/10.2833/203776.

[101] H. Wang, S. A. Pourmousavi, W. L. Soong, X. Zhang, and N. Ertugrul, “Battery and energy management system for vanadium redox flow battery: A critical review and recommendations,” *J Energy Storage*, vol. 58, p. 106384, Feb. 2023, doi: 10.1016/J.EST.2022.106384.

[102] M. Daniel, N. P. Byron, and C. M. Krowne, “Harnessing redox flow batteries for industrial applications: Opportunities and future directions,” *J Power Sources*, vol. 591, p. 233889, Jan. 2024, doi: 10.1016/J.JPOWSOUR.2023.233889.

[103] World Bank, “Circular Business Model for Vanadium Use in Energy Storage,” Washington D.C., Feb. 2024. Accessed: Jun. 01, 2024. [Online]. Available: https://documents.worldbank.org/en/publication/documents-reports/documentdetail/099020324185517458/p1740031e1bed00471a3c214deb8aa275af

[104] E. Commission, I. Directorate-General for Internal Market Entrepreneurship and SMEs, M. Grohol, and C. Veeh, *Study on the critical raw materials for the EU 2023 – Final report*. Publications Office of the European Union, 2023. doi: doi/10.2873/725585.

[105] B. R. Chalamala, T. Soundappan, G. R. Fisher, M. R. Anstey, V. V Viswanathan, and M. L. Perry, “Redox Flow Batteries: An Engineering Perspective,” *Proceedings of the IEEE*, vol. 102, no. 6, pp. 976–999, 2014, doi: 10.1109/JPROC.2014.2320317.

[106] Vanadium Price, “LIVE Vanadium Price, News and Articles,” Trade Silver Elephant. Accessed: Jun. 01, 2024. [Online]. Available: https://vanadiumprice.com/

[107] F. R. Brushett, M. J. Aziz, and K. E. Rodby, “On Lifetime and Cost of Redox-Active Organics for Aqueous Flow Batteries,” *ACS Energy Lett*, vol. 5, no. 3, pp. 879–884, 2020, doi: 10.1021/acsenergylett.0c00140.

[108] F. J. Vázquez Galván, “Redox flow batteries: From vanadium to earth abundant organic molecules (quinones),” Universitat de Barcelona, 2019.

[109] F. Gerard, L. Guevara Opinska, T. Smit, and K. Rademaekers, “Policy Support for Heating and Cooling Decarbonisation Roadmap,” Dec. 2021.

[110] U.S. Department of Health & Human Services, “Air Pollutants,” Centers for Disease Control and Prevention. Accessed: Mar. 18, 2024. [Online]. Available: https://www.cdc.gov/air/pollutants.htm

[111] IEA, “Net Zero Roadmap: A Global Pathway to Keep the 1.5 °C Goal in Reach,” Paris, 2023. Accessed: Feb. 27, 2024. [Online]. Available: https://www.iea.org/reports/net-zero-roadmap-a-global-pathway-to-keep-the-15-0c-goal-in-reach

[112] IEA, “Carbon Capture, Utilisation and Storage.” Accessed: Apr. 29, 2024. [Online]. Available: https://www.iea.org/energy-system/carbon-capture-utilisation-and-storage#how-does-ccus-work

[113] S. La Hoz Theuer and A. Olarte, “Emissions Trading Systems and Carbon Capture and Storage: Mapping possible interactions, technical considerations, and existing provisions,” Berlin, 2023. Accessed: May 04, 2024. [Online]. Available: https://icapcarbonaction.com/system/files/document/La%20Hoz%20Theuer%20%26%20Olarte%20%282023%29.%20ETSs%20and%20CCS_ICAP.pdf

[114] IEA, “ETP Clean Energy Technology Guide.” Accessed: Apr. 29, 2024. [Online]. Available: https://www.iea.org/data-and-statistics/data-tools/etp-clean-energy-technology-guide

[115] A. J. Lawson, “Carbon Capture Versus Direct Air Capture,” Apr. 2020. Accessed: Apr. 29, 2024. [Online]. Available: https://crsreports.congress.gov/product/pdf/IF/IF11501/3

[116] D. J. Tenenbaum, “Food vs Fuel: Diversion of Crops Could Cause More Hunger,” 2008. doi: https://doi.org/10.1289%2Fehp.116-a254.

[117] European Commission, “Waste Framework Directive.” Accessed: Apr. 12, 2023. [Online]. Available: https://environment.ec.europa.eu/topics/waste-and-recycling/waste-framework-directive_en

[118] European Commission, “Circular Economy.” Accessed: Apr. 22, 2023. [Online]. Available: https://environment.ec.europa.eu/topics/circular-economy_en

[119] European Commission and Directorate General for Communication, *Circular economy action plan: for a cleaner and more competitive Europe*. Publications Office of the European Union, 2020. doi: doi/10.2779/05068.

[120] R. Smith, *Chemical Process Design and Integration*. John Wiley & Sons, Ltd, 2005.

[121] N. Poli, C. Bonaldo, M. Moretto, and M. Guarnieri, “Techno-economic assessment of future vanadium flow batteries based on real device/market parameters,” *Appl Energy*, vol. 362, p. 122954, May 2024, doi: 10.1016/J.APENERGY.2024.122954.

[122] Sumitomo Electric, “Redox Flow Battery Brochure.” May 2024. Accessed: May 30, 2024. [Online]. Available: https://sumitomoelectric.com/sites/default/files/2024-04/download_documents/RFBcatalog_EN_202405.pdf

[123] J. Runyon, “SDG&E tests vanadium redox flow battery in zero-emission microgrid,” Power&Grid International. Accessed: Jun. 22, 2024. [Online]. Available: https://www.power-grid.com/energy-storage/sdge-tests-vanadium-redox-flow-battery-in-zero-emission-microgrid/#gref

[124] EASE, “Technical Description Flow Battery,” Brussels. Accessed: Jun. 15, 2024. [Online]. Available: https://ease-storage.eu/wp-content/uploads/2016/03/EASE_TD_FlowBattery.pdf

[125] W. Short, D. J. Packey, and T. Holt, “A Manual for the Economic Evaluation of Energy Efficiency and Renewable Energy Technologies,” 1995.

[126] R. Baxter and R. Byrne, “Energy Storage System Pricing,” in *U.S. DOE Energy Storage Handbook*, 2020. Accessed: Jun. 08, 2024. [Online]. Available: https://www.sandia.gov/ess/publications/doe-oe-resources/eshb

[127] Banco de España, “Tabla tipos de interés legal.” Accessed: Jun. 16, 2024. [Online]. Available: https://clientebancario.bde.es/pcb/es/menu-horizontal/productosservici/relacionados/tiposinteres/guia-textual/tiposinteresrefe/Tabla_tipos_de_interes_legal.html#

[128] Agencia Tributaria, “Tipo Impositivo,” Gobierno de España. Accessed: Jun. 16, 2024. [Online]. Available: https://sede.agenciatributaria.gob.es/Sede/impuesto-sobre-sociedades/que-base-imponible-se-determina-sociedades/tipo-impositivo.html

[129] Invinity Energy Systems, “INVINITY VS3-022 SIX PACK VANADIUM FLOW BATTERY,” Jan. 2023.

[130] IDAE, “Convocatoria para proyectos innovadores de I+D de almacenamiento energético,” Madrid, May 2022. Accessed: Jun. 25, 2024. [Online]. Available: https://sede.idae.gob.es/lang/extras/tramites-servicios/Almacenamiento_I+D/2022_05_03_FAQs_Almacenamiento_I+D.pdf

[131] red eléctrica, “Componentes del Precio Final y Energía del Cierre (€/MWh/MWh) Sistema Eléctrico Peninsular,” REData: Mercados. Accessed: Jun. 22, 2024. [Online]. Available: https://www.ree.es/es/datos/mercados/componentes-precio-energia-cierre-desglose?start_date=2023-06-01T00:00&end_date=2024-05-31T23:59&time_trunc=month&systemElectric=peninsular

[132] J. Girschik, L. Kopietz, M. Joemann, A. Grevé, and C. Doetsch, “Redox Flow Batteries: Stationary Energy Storages with Potential,” *Chemie Ingenieur Technik*, vol. 93, pp. 1–12, Feb. 2021, doi: 10.1002/cite.202100001.

[133] A. Colthrope, “First phase of 800MWh world biggest flow battery commissioned in China,” Energy Storage News. Accessed: Jun. 23, 2024. [Online]. Available: https://www.energy-storage.news/first-phase-of-800mwh-world-biggest-flow-battery-commissioned-in-china/

[134] StorEn Technologies Inc., “StorEn About US.” Accessed: Jun. 23, 2024. [Online]. Available: https://www.storen.tech/

[135] Primus Power, “Primus Power Product.” Accessed: Jun. 23, 2024. [Online]. Available: https://primuspower.com/en/product/

[136] Quino Energy, “Quino Energy About Us.” Accessed: Jun. 23, 2024. [Online]. Available: https://quinoenergy.com/

[137] KEMIWATT, “KEMIWATT About Us.” Accessed: Jun. 23, 2024. [Online]. Available: https://kemiwatt.com/#

[138] Flow Batteries Europe, “About Flow Batteries Europe.” Accessed: Jun. 24, 2024. [Online]. Available: https://flowbatterieseurope.eu/about-flow-batteries-europe/

[139] IRENA, “Capacity and Generation - Country Rankings,” Data. Accessed: Jul. 02, 2024. [Online]. Available: https://www.irena.org/Data/View-data-by-topic/Capacity-and-Generation/Country-Rankings

[140] Direção Geral de Energia e Geologia, “Integrated National Energy and Climate Plan (NECP) 2021-2030,” Dec. 2019. Accessed: Jul. 02, 2024. [Online]. Available: https://climate-laws.org/documents/national-energy-and-climate-plan_d291?id=portugal-s-national-energy-and-climate-plan-for-2021-2030_47f6