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Carnot battery technology: A state-of-the-art review

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ABSTRACT

The growth of renewable energy requires flexible, low-cost and efficient electrical storage to balance the mismatch between energy supply and demand. The Carnot battery buffers electrical energy by storing thermal energy (charging cycle mode) from a resistive heater or a heat pump system when the electricity production is higher than the demand. When electricity demand is higher than the production, the Carnot battery generates power from the stored thermal energy (power cycle mode). This paper is a review of this emerging and innovative technology, including a market analysis. First, the different possible technologies and configurations of Carnot batteries are described. This includes charging cycles, power cycles and thermal energy storage systems. Furthermore, a state-of-the-art of the existing prototypes in the world is given. The performance indicators for this technology are unclear, and this paper tries to define objective performance indicators. Finally, all the described technologies are compared, and conclusions are drawn to help engineers select the optimal technology for a given case.

1. Introduction

1.1. Renewable energy and grid flexibility

The requirement to grow the share of deployed Renewable Energy Sources (RES) in the electricity grid goes hand in hand with the need of improving the electric system flexibility [1,2]. This challenge may be tackled from different angles on both the demand and production sides. Next to demand-side management (DSM), increasing the energy storage capacity in the grids is a proven strategy. As is already known, such a task may be not trivial, as in most of the mature electric systems the easily-exploitable additional capacity for Pumped Hydro Energy Storage (PHES) is nearly exhausted [3]. PHES is the only grid-scale Electric Energy Storage (EES) technology that has proven to be technically and economically viable up to the present day. Now we are looking for alternative EES technologies, several of which having been recently developed, proposed or re-discovered.

Different EES technologies are each based on different physical principles and thus have different characteristic performance indicators, such as power-to-capacity ratios, charge and discharge response times, different energy/power-to-volume ratios and different specific costs per *kW* and per *kWh* [4]. Owing to these differences, each EES technology has an application niche best suited for it, and several niches have already found their most suited EES. The electric systems future outlooks [5] predicts that the residual demand curve (commonly known as “duck curve” [6,7]) will be the most affected by the solar PV production pattern (i.e. maximum production in the central day hours). In order to shift massive amounts of energy from daylight hours to other parts of the day, a storage fleet that can charge at nominal power for several hours per day will be needed. In other words, grid-scale systems, mainly oriented towards long duration (from 4 to 8 *h*), will be required. In this context, as the required power-to-capacity ratios *(kW/kWh*) would be very low (from at least 1/4 h^{-1} and lower), the EES storage medium and system must be as cheap as possible. For the moment, this requirement rules out the well-established EES technology based on lithium chemistry batteries. However, these may come back into play as their cost per *kWh* is falling, which is expected to continue in the future [8]. As for today, some of the largest non-PHES EES installations are actually represented by lithium battery systems, like in Australia, where a 100 MW / 129 MWh system was installed in 2018 [9]. However, this system is designed for providing ancillary services, as the nominal power-to-capacity ratio is not suited for long-

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Nomenclature

E	Electrical energy [Wh]
El	Electrical
Q	Thermal energy [Wh]
V	Volume [m^3]

Acronym

CAES	Compressed Air Energy Storage
CB	Carnot battery
CHEST	Compressed Heat Energy Storage
COP	Coefficient Of Performance
EES	Electrical Energy Storage
HE	Heat Engine
HP	Heat Pump
HT	High temperature
HVAC	Heating and Ventilation Air Conditionning
LAES	Liquid Air Energy Storage
LCOS	Levelized Cost of Storage
LNG	Liquefied Natural Gas
LT	Low Temperature
ORC	Organic Rankine Cycle
PCM	Phase Change Material
PEG	Polyethylene glycol
PHES	Pumped Hydro Energy Storage
PTES	Pumped Thermal Electricity Storage
RC	Rankine Cycle
RES	Renewable Energy Source
STES	Sensible Thermal Energy Storage
TCES	Thermochemical Energy Storage
TES	Thermal Energy Storage
TI	Thermally Integrated
TRL	Technology Readiness Level

Greek

ε	Efficiency [-]
η	Efficiency [-]
γ	Compactness
τ	Time [h]

Subscripts

ch	Charge
cv	Constant volume
dis	Discharge
e	Energy
ext	External
in	Inlet
II	Second law
max	Maximum
min	Minimum
rt	Roundtrip
w	Power
0	Reference

duration load shifting. This confirms that lithium batteries are not limited by the size they can reach, and it is mainly the cost-per-capacity unit that holds them back from being used for low power-to-capacity ratio applications.

The requirement of using an inexpensive storage medium called attention to alternative storage concepts, even though in most cases the efficiencies are not comparable with those featured in batteries. The technologies that are attracting most attention are [10–13]: Compressed Air Energy Storage (CAES); alternative versions of PHES, based on using seawater or underground reservoirs; battery technologies based on molten sodium salt and liquid electrolytes (i.e. flow batteries); Liquified Air Energy Storage (LAES) [14] and finally, the technology group named Carnot Batteries.

Carnot batteries include technologies like Pumped Thermal Electricity Storage (PTES) [11], the systems based on the use of electric heaters and Rankine or Brayton heat engines and, in extension, also LAES. Including LAES into the Carnot battery group may be seen as a controversial choice. Therefore, a detailed argument supporting this choice will be provided further on in Section 1.2.

In Carnot batteries, electric energy is stored as thermal energy, which is later recovered during discharge. The charging can be done with different heating technologies, whereas the discharging can be done with different thermal engine technologies [11]. Carnot batteries are based on several patents dating as far back as 1979 [11], but the original concept was proposed in 1922 by Marguerre [15], whereas other authors trace the origin of PTES back to the work of John Ericsson in 1883 [11].

As Carnot batteries are based on heat pumps and heat engines, they are made up of pumps, compressors, expanders, turbines and heat exchangers, which are all components that may be easily scaled up. For this reason, Carnot batteries might be an alternative to PHES and CAES. Compared to these, Carnot batteries might have lower efficiencies, but they do not rely on pre-existing reservoirs and caves, which may give them an advantage over PHES and CAES as they can be installed everywhere. Carnot batteries' geographical independence stems from the fact that, as opposed to CAES, energy is stored as heat and not as pressure, even though a slight pressurisation of the reservoirs might be required. However, low operating pressures allow the Carnot batteries' thermal tanks to be artificially built, and any location could be potentially exploited.

Among the grid-scale EES technologies, Carnot batteries have the lowest average technology readiness level (TRL), even though they are becoming more and more popular. For this reason, the actual potential of this heterogeneous technology group is still unclear, despite the relevant research currently being carried out. Lately, a significant amount of publications have been dedicated to Carnot batteries. Furthermore, several prototypes have been developed, or are currently being developed, to prove the promising theoretical results which were recently derived in this field (see Section 4.1.2). In this phase, it is relevant to collect the main contributions on the topic to provide the reader with an idea of what is the state-of-the-art for Carnot batteries. This paper thus contains a discussion on Carnot battery technology, including storage technologies, a clear definition of Carnot battery performance indicators. Furthermore, the existing prototypes are listed and their respective performance parameters are reported. Finally, the financial and market outlook for Carnot batteries are reviewed.

1.2. Definition

Carnot batteries include several technologies and it is difficult to provide a definition that encompasses all their nuances. To the best of the authors' knowledge, this is the first attempt to provide a systematic criterion to decide whether a technology is a Carnot battery or not. Therefore, the study may be an essential contribution for future scientific work and policies.

A Carnot battery is an EES technology. Therefore, there should always be at least an electric input and an electric output. A Carnot battery performance may be improved by using additional thermal energy inputs in the charge or discharge phases, but this should not change its primary purpose, which is storing *electric* energy. Similarly, a

Carnot battery may produce both electric energy and *useful* thermal energy. However, the electric output must be comparable with the electric input. In other words, electric heating alone should not be considered a Carnot battery.

A comprehensive Carnot battery definition could be as follows:

A Carnot battery is a system primarily used to store electric energy. In a Carnot battery, the electric energy (input) is used to establish a temperature difference between two environments, namely the low temperature (LT) and high temperature (HT) reservoirs. In this way, the storage is charged, and the electric energy is stored as thermal exergy. As the heat flows against the thermal gradient, work is spent to charge the storage. In the discharge phase, the thermal exergy is discharged by allowing the heat flowing from the HT to the LT reservoir. The heat flow powers a heat engine (HE) which converts it into work and discharges the residual heat into the LT reservoir. In this way, a fraction of the electric input is recovered. This definition is illustrated in Fig. 1.

In practice, the described operation may be realised with several different technologies. The HT and LT reservoir could be actual physical tanks, filled with gas, liquid, solid or changing-phase materials. Otherwise, one of the two reservoirs could be missing, and its role may be taken up by the environment.

The absorbed specific work increases, for a fixed amount of charged thermal exergy, with the temperature difference between the HT and LT reservoirs. Similarly, the recovered specific work decreases as the temperature difference between the reservoirs is reduced. However, additional heat sources and heat sinks may be used to reduce, or increase, the operating temperature differences during charge or discharge (i.e. they act as thermal exergy additional sources) (Fig. 1). Exploiting additional heat sources may improve the Carnot battery performance from a purely electric point of view. However, as additional energy sources are exploited, different performance metrics should be used.

In the charge, electric energy is used to move the heat from the LT to the HT reservoir. Such a task may be done with a traditional heat pump (HP), an electric heater, or any other technology. Likewise, in the discharge, any heat engine technology may be used, ranging from Rankine, Brayton, or different thermodynamic cycles, to thermoelectric generators.

The definition of Carnot batteries is useful to understand why LAES, for example, is a Carnot battery, whereas other similar technologies, like CAES, are not. In LAES, the electric input is used to liquefy air. In general terms (Linde process), such a task is performed by compressing the air and by cooling it with a pre-cooling and an expansion until liquefaction occurs. The air is not stored under pressure, so no mechanical energy is stored alongside the thermal exergy associated with the air vaporisation heat. From the Carnot battery point of view, the liquefaction apparatus is just a (very) sophisticated heat pump, which cools down the air. During discharge, the air is compressed, vaporised (the required heat may come from the stored compression excess heat, the environment or any additional heat sources) and expanded in a turbine. In other words, during LAES discharge, an air HE is operated. This operational pattern perfectly reflects the Carnot battery one.

Alternatively, for CAES, the energy is mostly stored as mechanical energy, by compressing the air. In CAES, the compression heat is just rejected into the environment, and, even if it is stored, like in adiabatic CAES, it represents the minority of the stored energy. Therefore, the difference lies in the form under which the electric energy is stored (mechanical versus thermal). Even though several Carnot battery technologies require a compression step during the charge phase, like CAES does, the mechanical energy is immediately recovered, by expanding the fluid to cool it down, which does not happen in CAES.

1.3. Possible Carnot battery configurations

One of the significant subgroups that can be clearly identified within the heterogeneous group of Carnot batteries is PTES, also called PHES (Pumped Heat Energy Storage) or CHEST (Compressed Heat Energy Storage). Here, the "PTES" acronym will be used, as "PHES" is often used for "pumped hydro" in literature. PTES is divided into two main branches: the first one is based on direct and inverse Brayton systems, whereas the second one is based on direct and inverse Rankine systems [11]. Other cycles and variants are possible, like the Lamm-Honigman process, and are discussed in this Section 1.3.3 (Fig. 2).

In the following overview and in the technical discussions, if the efficiency is discussed, the round trip efficiency, as defined in Section 2, is meant. If this is not the case, this will be clearly stipulated in the text.

1.3.1. Brayton

A Brayton Carnot battery, i.e. a Brayton PTES, is usually comprised of a Brayton heat pump and a Brayton heat engine. The heat pump operation is based on an inverse Brayton cycle with two sensible heat thermal reservoirs (HT and LT). Given this layout, the complete EES usually contains two thermal reservoirs and four machines (two compressors and two expanders). A more straightforward configuration (Fig. 3) is proposed when only two turbomachines are used [16]. Another possibility is to use a two-piston machine [17]. The principle is simple. During the charging mode, the heat is transferred from the LT reservoir to the HT reservoir through the compression of a gas (the compressor uses more energy than the expander). However, during the discharge phase, the pressure difference between the HT and the LT

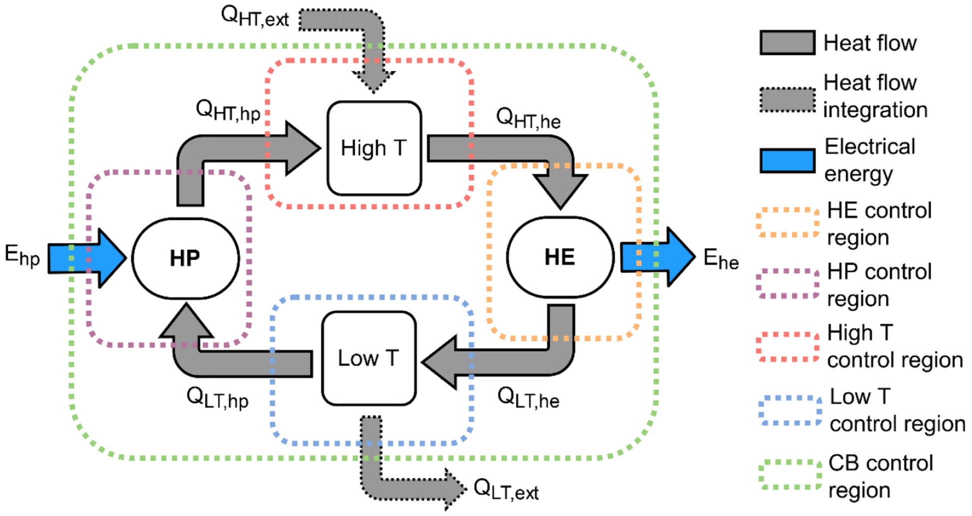

Fig. 1. Carnot battery definition.

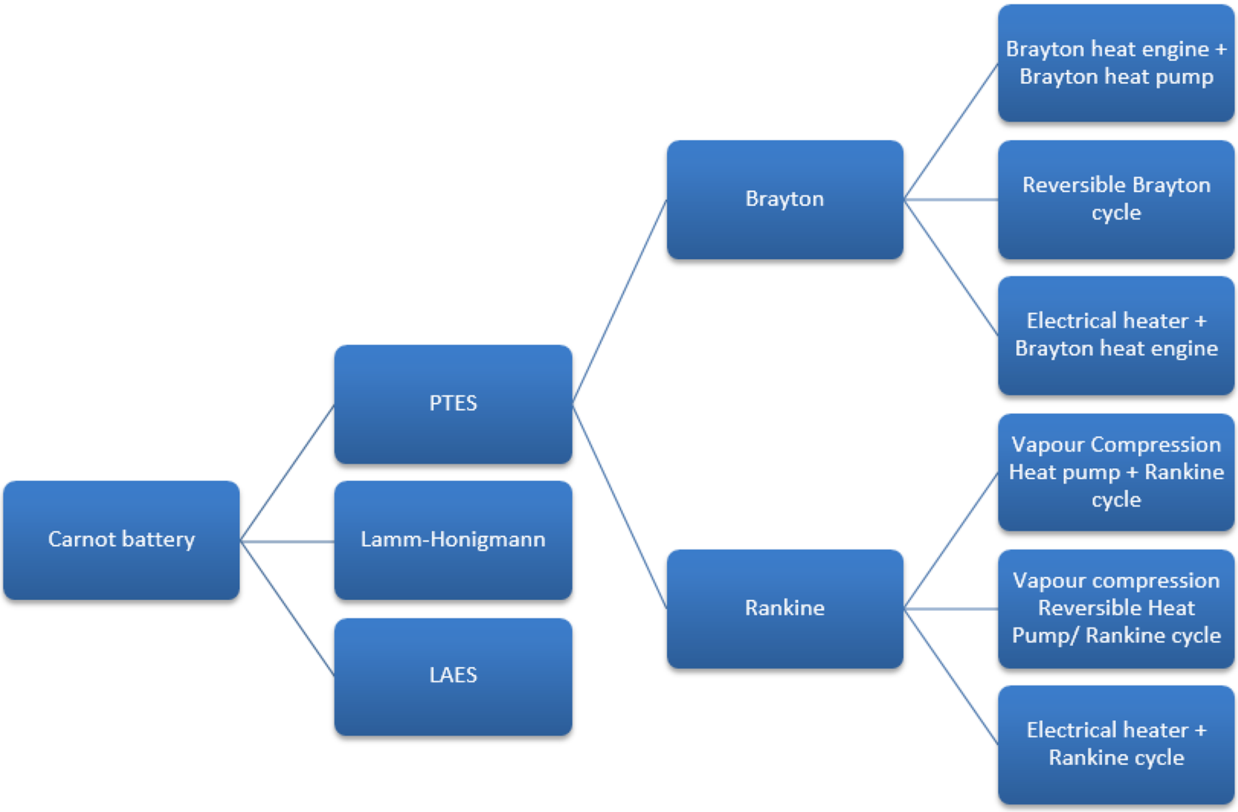

Fig. 2. Possible configurations for a Carnot battery.

reservoir is used to entrain the expander (the turbine work is higher than the compressor energy use). It should be noted that the combination of an electrical heater and gas cycle has also been considered, but with rather low round-trip efficiencies (40–50%) [18].

Apart from these, due to compression and expansion irreversibility, it is usually impossible to perfectly match compression/expansion inlet/outlet temperatures between charge and discharge cycles. In this case, heaters and coolers may be used to adjust machine outlet conditions. In this way, the heat generated by irreversibilities is discharged to the environment, and the storage may operate in a cyclic behaviour [18].

For Brayton PTES, both dynamic [19] and volumetric machines [20] may be used. By using a volumetric compressor/expander, a reversible machine may be more easily adopted [17,20], which may result in lower global performance, but also in lower capital costs.

A classic Brayton PTES layout can be found in [19]. This system may be considered to be representative of Brayton PTES features: the maximum temperature is 1000°C (HT reservoir), while the minimum temperature is -70°C (LT reservoir); compression/expansion ratio is low, around 4.6, and efficiency is in the range of 60 – 70%. The most common working fluid is argon, even though, with air, a higher efficiency may be obtained [11]. Nonetheless, in [21] it is demonstrated that efficiency is related to the temperature ratio, rather than to the pressure ratio. Furthermore, pressure must be low, to reduce the storage tanks costs, and argon can reach higher temperatures for equal storage pressure ratios. Brayton PTES is most often based on packed bed sensible heat storage. It is worth noting that, while round-trip efficiencies of around 60 – 70% are often claimed in the literature, these values are calculated with very high compressor/turbine polytropic efficiencies, which are over 90%. The efficiency of Brayton PTES is extremely sensitive to machine polytropic performance, such that if slightly lower figures are used, a round-trip efficiency of around 27 – 35% can be found [11,17]. To date, the only working Brayton PTES demonstrator reported very low efficiency [20]. Better results are expected for larger applications, as in [17], where a conservative theoretical efficiency estimation gave 52% as a result of a 2 MW/16 MWh system.

Despite the lower efficiency, if compared to batteries or PHES, Brayton PTES systems are interesting due to their high energy density (up to 200 kWh_{th}/m^3) and very low estimated capacity prices (50 – 180 €/kWh [22] and 12 – 22 €/kWh) [17], which may result in an

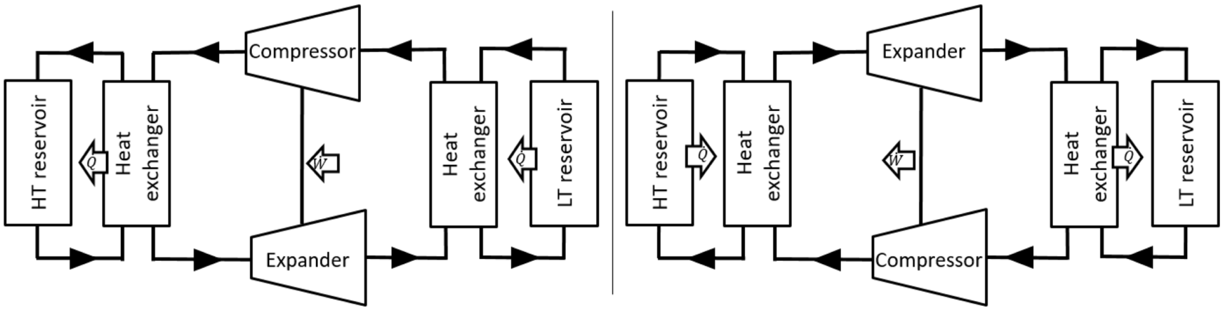

Fig. 3. Reversible Brayton cycle (left: charging, right: discharging).

economically feasible application.

Due to Brayton PTES' high HT reservoir operating temperatures, which are usually well above 200°C, it may be difficult to integrate additional low-grade (i.e. low temperature) thermal energy inputs in such systems. Therefore, proposed modifications are integration with cryogenic waste energy in the LT reservoir [23], or with electric heaters, as in [24]. The use of electric heaters may fulfil part of the charging process, raising the operating fluid temperature before the HT reservoir inlet. In this way, the outlet temperature of the charge phase compressor could be lowered. This may be beneficial from a technological point of view, as currently there are few compressor technologies able to withstand the high discharge temperature imposed by classical Brayton PTES architecture [19,25], especially if high polytropic efficiencies are needed. The problem posed by a high compressor discharge temperature has been recognised by some authors, who propose a compressor discharge temperature of around 500°C [17,26]. Such discharge temperatures are near to the current technical limitation and are achieved in the modern aero-derivative gas turbines.

1.3.2. Heat pump and Rankine cycle

1.3.2.1. Classical HP/RC power system. The second branch of PTES technology is based on Rankine cycles. Rankine PTES could be a valid alternative to the Brayton cycle because it generally achieves higher energy densities and it stores energy at a much lower temperature. This is beneficial for thermal losses and the choice of reservoir/machines materials, and it might allow for the use of phase change materials as a storage medium. Maximum efficiencies achieved by the Brayton and Rankine systems are similar (62%-65%) [26,27].

Rankine PTES is mostly based on trans-critical and supercritical CO_2 cycles [28,29], where an efficiency of 53% can be achieved by storing energy at 123°C. The basic system is improved in [25], by optimising the thermal layout of the system. In [26,29], both LT latent storage (ice-based) and HT sensible storage (liquid-based) are used. Further improvements are found in [28], where a liquid piston is used to allow the system to perform a nearly-isothermal compression and expansion. In this way, the compression work is reduced, and the expansion work is increased. The compression heat in excess is stored for later use during the expansion.

A different concept may be found in [29], where LT and HT reservoirs are based on the underground thermal storage concept. In other words, geothermal heat exchangers are used to store thermal energy on the ground. Despite the efficiency being around 40–60%, depending on the investigated layout, the financial implication of using geothermal heat exchangers, which are usually very costly, should be carefully investigated.

Rankine PTES may also be based on different operating fluids. In literature, several examples of PTES systems based on Water, Ammonia or refrigerants can be found. In [30], a cascaded NH_3/water vapour compression heat pump is used for charging a hybrid sensible/latent heat storage. Given the temperature reached by the system, the discharge phase is performed with a water-steam cycle. The expected round-trip efficiency is around 73%. Similarly to Brayton PTES, Rankine PTES' round-trip efficiency is strongly affected by compressor and turbine polytropic efficiencies. Thus, values equal to 0.9 were used in [30] to achieve satisfactory results.

Other examples of Rankine PTES using natural or synthetic refrigerants may be found in [30–39]. All the systems investigated in these papers are based on the use of vapour compression Heat Pumps (HP) and Organic Rankine Cycles (ORC). Compared to Brayton and Rankine systems presented previously, the latter uses refrigerants as working fluids with more conventional equipment that is readily available. By directly using available commercial equipment, *MW* scale systems may potentially be built without many challenges. For larger applications, multiple HP and ORC could be used in parallel, given the modular structure of these systems.

For Rankine PTES, the use of solids as storage media is not cited in the literature. The operating temperatures and the nature of the heat absorption and rejection transformations push for the use of phase change materials, especially for the LT reservoir, where ice storage may be used [40]. In supercritical CO_2 systems, if the heat is absorbed from and rejected to the LT storage at a constant temperature (CO_2 evaporation and condensation), then a phase change material may be suited. On the other hand, if the heat is absorbed from and rejected to the HT reservoir with a significant temperature glide (CO_2 cooling in gas coolers/heaters), then a sensible liquid heat storage may be used. Rankine systems that operate with refrigerants are usually subcritical, and so phase change materials may be used for both the HT and LT reservoir. Furthermore, as in vapour compression heat pumps the condensation heat load can be both with and without temperature glide, a hybrid sensible/latent thermal storage may be used, as in [31,35].

An interesting concept for improving Rankine PTES performance is to exploit additional heat sources and heat sinks (as detailed in Section 1.3.4). This technique is especially convenient if low-grade, or waste heat sources are used. Integration of low-temperature thermal energy is easier in Rankine PTES systems due to the operating temperature levels, which are often lower than 200°C. A similar integration is more difficult in Brayton PTES due to the high operating

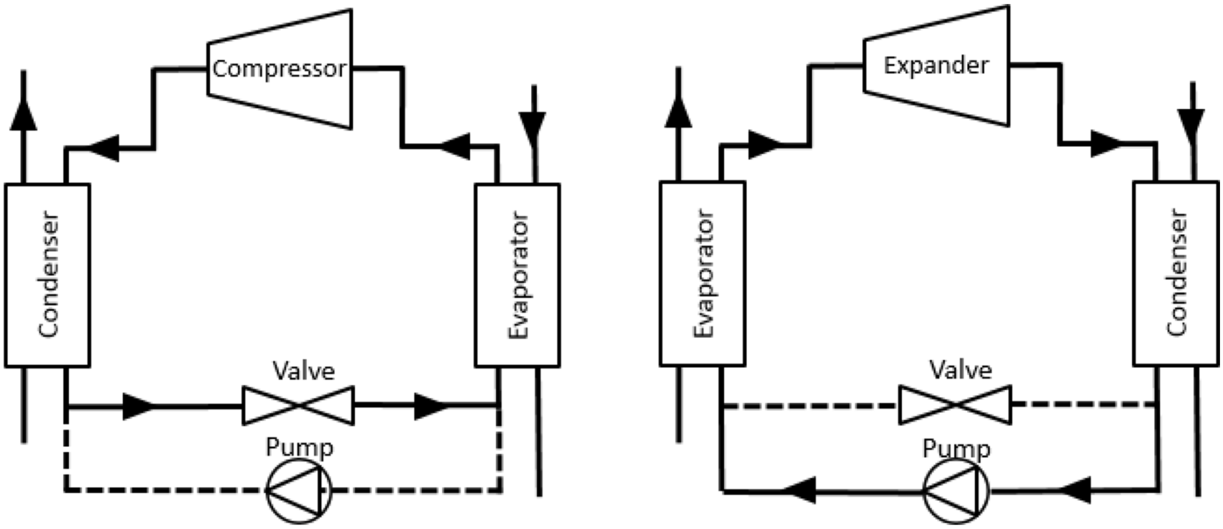

Fig. 4. Reversible HP/RC system (left = heat pump mode, right = RC mode) [45].

temperatures, as pointed out in Section 1.3.1.

1.3.2.2. Reversible HP/RC power system. Many similarities were observed between a heat pump (HP) and a Rankine Cycle (RC) for small-scale application (volumetric machines, refrigerants, heat exchangers). Based on this observation, a system able to work as a heat pump or as an RC with the same components may be conceived, i.e. a reversible HP/RC system (Fig. 4). Its application for a small-scale Carnot battery is straightforward and would significantly decrease investments due to the use of a single machine instead of the combination of a heat pump and an ORC power system. This system presented many possible applications [41] and was studied theoretically for the automotive sector [42], data centre [40], stationary engine [43] and Net Zero Energy Buildings [44,45].

Finally, several prototypes have been built to prove the feasibility of such technology (Table 1). In this table, inverted architecture refers to the architecture of Fig. 4, where the condenser and evaporator are exchanged. In the classical architecture, each heat exchanger conserves its role [46].

Further information can be found about the inherent constraints of the system, the modelling, the optimal sizing and mappings of performance as a function of temperature levels [39,41].

1.3.2.3. Electrical heater combined with a Rankine cycle power system. It might be interesting to store heat at high temperatures to increase the compactness of a Carnot battery. This may induce a low coefficient of performance (down to 1) if a heat pump is used for the charging process. Therefore, it might be interesting to use an electrical heater, which is usually cheaper and simpler than a heat pump. Two options have been proposed so far: the use of an electrical resistance [50] or the use of a rotating heater (asynchronous machine with permanent magnet using induction). The main advantage of the latter option is that the resistance and the AC/DC converter are not needed compared to the former [51]. Three configurations are possible:

- A GWh-scale stand-alone solution. In this case, the system would be able to store and supply electricity, process steam and heat independently of geographical conditions.
- New flexibility for existing heat cycles. It is attached to a fossil fuel power plant or an energy-intensive industrial plant.
- A second life for power plants. Thermal fossil fuel power stations can be transformed into storage plants, combining existing equipment with the new technology [50].

1.3.3. Lamm-Honigmann-process

The Lamm-Honigmann process is a thermochemical energy storage invented in the 19th Century [52]. In general, the storage system can be charged with the input of heat or mechanical work and discharged with the release of heat, LT or mechanical work. The discharging process is achieved through the heating of a solution of water and another liquid (LiBr or NaOH typically) presenting different vapour pressure. Due to the difference in the vapour pressure, an expansion machine can be operated by steam flowing from a water vessel to a solution vessel (Fig. 5). Recharging can be accomplished with the input of heat to desorb the water out of the aqueous solution. The water vapour will be condensed at a lower temperature, to recover the water and maintain a closed cycle, [53].

One advantage of the technology is the absence of self-discharge (except for minor heat losses). An in-depth analysis of the process is missing thus far, although recent studies show the growing interest in the technology [53].

1.3.4. Thermally integrated Carnot batteries (waste heat integration)

Typically, the round-trip efficiency (ε_{rt}), defined as the electrical energy output (discharge) divided by the electrical energy input (charge), is below 70% for a standard Carnot battery. This low round-trip efficiency is the reason why it can be helpful to valorise waste heat streams in the system to improve its performance (thermally integrated Carnot battery). Some authors expect more than 100% roundtrip efficiency [31,35,38]. When using a thermally integrated Carnot battery, two different options are possible for the thermal energy storage: the HT and the LT configurations (Fig. 6).

On the one hand, the HT storage configuration uses a heating system (heat pump in this example) to increase the waste heat temperature. This allows the power cycle (RC in this example) to increase its efficiency by working with a higher temperature difference. On the other hand, the LT storage configuration stores thermal energy at temperatures lower than the ambient (through a vapour compression cycle in this example). Only a few references discuss this possibility [35,38,40]. Once again, it allows the power cycle to work efficiently with a higher temperature difference. From a thermodynamic point of view, it can be shown (analytically or with a constant efficiency model) that the round-trip efficiency is always higher for the HT storage configuration [38]. This does not mean that the LT storage cannot present other advantages (a more straightforwrd use of latent energy storage, for example).

As will be pointed out in Section 2, the concept of exploiting additional heat sources and sinks is primarily linked to Rankine systems due to the operating temperature range. For Rankine systems, the thermal integration concept can be found in [25,54], and was analysed in-depth in [31,32,38], where the HT storage integration was investigated for a heat pump/RC system and for several potential operating fluids. In these papers, the low-grade heat source is used to eliminate the LT reservoir. A similar idea is explored and expanded upon in [36, 38, 55,56, where a solar pond represents the heat source. The opposite can also be done, and the heat from solar energy can be used to replace the HT reservoir while maintaining the LT one [33,35].

Even though the integration of additional heat sources is particularly suited to Rankine systems, the same concept may also be applied to Brayton systems, as in [23], where cryogenic waste energy from LAES plants is recycled in a Brayton PTES system. Furthermore, the same concept has been extensively used in LAES applications, where the discharge phase is often powered by a waste heat load [14] to improve the electric discharge efficiency.

Two recent papers [38,55] showed the constraints in the sizing of a thermally integrated Carnot battery. Three constraints have to be taken into account: the energy density, the round-trip efficiency and the correct exploitation of the heat source. The main parameter to optimise is the storage temperature lift, i.e. the temperature difference between the completely charged thermal storage and the completely discharged thermal storage. If the thermal storage lift is high, the round-trip efficiency is low, whereas the waste heat exploitation and the energy

Table 1
State-of-the-art reversible HP/ORC systems.

Year	Application	Architecture	El. power	Fluid	References	Status
2015	Solar building	classical	4 kW	R134a	[47]	Finished
2016	Stationary engine	Inverted	8 kW	-	[43]	Ongoing
2019	Automotive	Inverted	1 kW	R134a	[48]	Finished
2019	Carnot battery	Inverted	2 kW	R1234yf	[40]	Ongoing
2019	Carnot battery	Inverted	1 kW	R1233zd	[49]	Ongoing

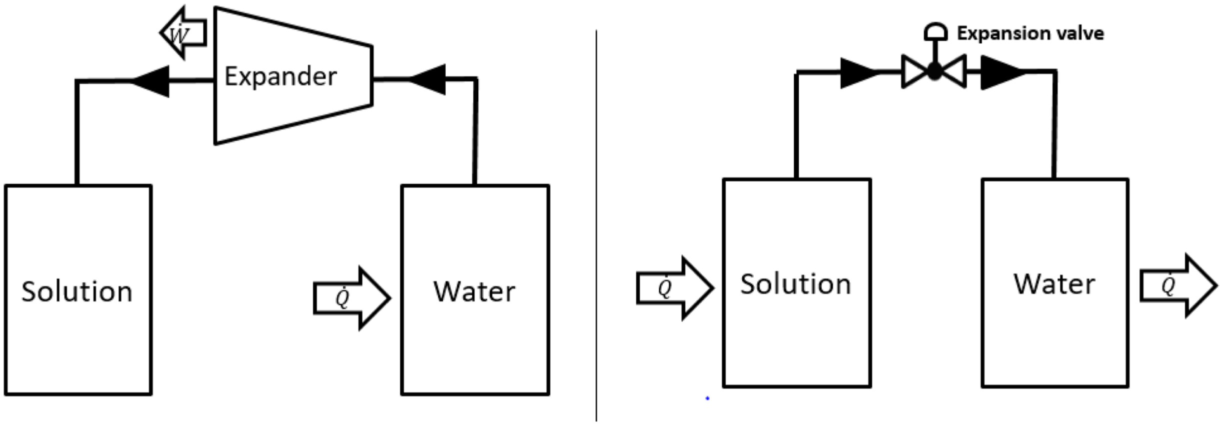

Fig. 5. Lamm-Honigman process (left: discharge, right: charge).

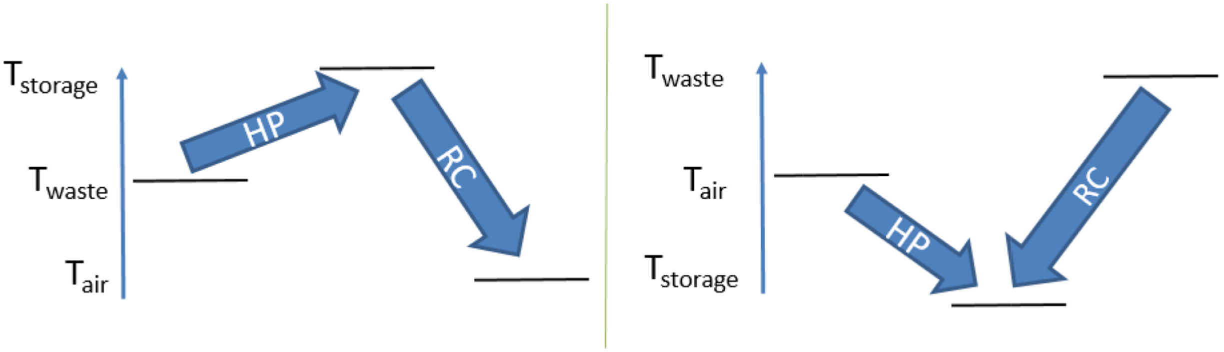

Fig. 6. Thermally integrated Carnot battery (left = HT storage, right = LT storage). Illustration with a heat pump and a Rankine cycle.

density are high, and vice versa.

2. Performance indicators

Several indicators may be used to characterise a Carnot battery performance. As an EES technology, the most widespread and useful performance indicator for a Carnot battery is the round-trip efficiency (RTE) ε_{rt}. This is defined as the ratio between the net electrical energy output E_{he} and the gross electrical energy input E_{hp}. The terms "net" and "gross" refer to the fact that the electrical energy input and output are subjected to losses in electrical components like generators, motors, converters, inverters, transformers and so forth. The energy input must be considered *before* these losses (gross input), whereas the energy output must be considered *after* (net output).

By referring to a generic Carnot battery, such as the one represented in Fig. 1, and by applying the energy balance to the closed system of Carnot Battery (green dotted line), with ΔU the variation of the internal energy of the system at constant volume (CV) (and excluding any external heat transfer):

During charging,

$$E_{hp} = \Delta U_{CV,charge} \tag{1}$$

During discharging,

$$\mathrm{E_{he}} = \Delta \mathrm{U_{CV,discharge}} \tag{2}$$

The round trip efficiency ε_{rt} is defined as the ratio of the delivered work to that put into the CB,

$$\varepsilon_{rt} = \frac{E_{he}}{E_{hp}} \tag{3}$$

This ratio can be higher than 1, if waste heat is included in the system (as further discussed). It would probably be more suitable and rigorous to call this "electrical energy ratio" instead of "efficiency". However, the word "efficiency" will be used in this paper since most of the literature refers to this name.

If the energy balance is applied on the Heat Pump from Fig. 1 (HP control region - purple dotted line – Eq. 4 and Heat Engine (HE control region – orange dotted line – Eq. 5) this gives a relation between the thermal energy of the system (Q) and the energy of the heat pump and heat engine:

$$E_{he} = Q_{HT,he} - Q_{LT,he} \tag{4}$$

$$E_{hp} = Q_{HT,hp} - Q_{LT,hp} \tag{5}$$

The Coefficient Of Performance (COP) of the heat pump and the efficiency of the heat engine can be calculated via Eqs. 6-7.

$$COP_{hp} = \frac{Q_{HT,hp}}{E_{hp}} = 1 + \frac{Q_{LT,hp}}{E_{hp}} \tag{6}$$

$$\eta_{he} = \frac{E_{he}}{Q_{Ht,he}} = \frac{1}{1 + \frac{Q_{LT,he}}{E_{he}}} \tag{7}$$

And thus,

$$\varepsilon_{rt} = \frac{E_{he}}{E_{hp}} = \frac{Q_{HT,he} - Q_{LT,he}}{Q_{HT,hp} - Q_{LT,hp}} \tag{8}$$

The definition in Eq. 8 may be used directly to calculate ε_{rt} from the heat pump and heat engine thermodynamic cycles, as in [18,20], among others. However, it could be interesting to relate ε_{rt} to heat pump and heat engine common performance indicators, such as COP_{hp} and η_{he}.

If fully reversible heat pumps and heat engines are used, and the heat transfer to the storage systems is reversible (thus happening without temperature difference), so no internal energy is accumulated, $\varepsilon_{rt} = 1$.

In real cycles, with all kinds of irreversibilities, $\varepsilon_{rt} < 1$. This can be linked to the exergy content of heat. Although energy is conserved in any conversion process, the work that can be produced by a heat flow is limited by the exergy of this heat flow.

This is true for all the systems without external heat addition. In case an additional energy (heat) input is provided to the system, this can provide an additional exergy stream that could counterbalance the losses due to irreversibilities.

These obvious considerations actually have an interesting consequence for the Carnot battery efficiency calculation. If again, the control volume around the battery is considered (dotted line, green – Fig. 1), and taking into account internal energy is stored inside the system the energy balance becomes (Eq. 9):

$$E_{hp} = E_{he} + \Delta U \tag{9}$$

where ΔU is a generic internal energy accumulation term.

This internal energy storage can be attributed to the HT an LT reservoir so the internal energy can be written as Eq. 10.

$$\Delta U = \Delta U_{HT} + \Delta U_{LT} \tag{10}$$

From Eqs. 9 and 10,Eq 11 is obtained.

$$E_{hp} = E_{he} + \Delta U = E_{he} + \Delta U_{HT} + \Delta U_{LT} \tag{11}$$

Two cases may be stated (Eq. 12).

$$\begin{cases} \varepsilon_{rt} = 1 \rightarrow E_{hp} = E_{he} \rightarrow \Delta U = \Delta U_{HT} + \Delta U_{LT} = 0 \\ \varepsilon_{rt} < 1 \rightarrow E_{hp} > E_{he} \rightarrow \Delta U = \Delta U_{HT} + \Delta U_{LT} > 0 \end{cases} \tag{12}$$

In other words, if a non-ideal storage is used (i.e. $\varepsilon_{rt} < 1$), heat accumulates as internal energy in the system. This precludes a system cyclic behaviour, and the storage system initial conditions cannot be re-established after discharge. This is a well-known problem, as several authors faced this issue in practice. In such cases, two additional components (typically an auxiliary heat pump and a heat exchanger, or two heat exchangers) were added to the EES, the purpose of which was to remove the excess heat from the LT and HT reservoir, thus restoring the CB initial conditions before the next charge/discharge cycle (see [18,21,24,27,56], for example). The commonly-proposed idea is to design the system in such a way that all the excess heat is accumulated in only one of the two heat reservoirs. This allows one of the two additional pieces of equipment used to restore the storage's initial conditions to be cut [18]. In this case, it must be decided whether the excess heat is accumulated in the HT or LT reservoir. This choice impacts on the way in which ε_{rt} may be expressed as a function of COP_{hp} and η_{he}, and on the ε_{rt} numerical value itself, as one of the two configurations is more efficient than the other.

Let the first configuration be the one in which the heat is accumulated *only* in the HT reservoir, i.e. $\Delta U_{HT} = 0$. Without loss of generality, the adiabatic reservoir hypothesis may be dropped, to account for CB thermal losses during energy storage period. Thermal losses may be expressed by means of a Thermal Energy Reservoir (TES) efficiency η_{tes}. If the HT reservoir is considered, η_{tes} accounts for the heat losses towards the environment, whereas, if the LT reservoir is considered, η_{tes} accounts for the heat leakage from the environment towards the reservoir. As discussed earlier, a share of the reservoir-stored exergy is lost during the energy conservation period, for both the HT and LT reservoir.

By using the control volume on the HT storage system (dotted line, red – Fig. 1), the following equations may be written (Eq. 13):

$$\Delta U_{HT} = \eta_{tes} \cdot Q_{HT,hp} - Q_{HT,he} = 0 \tag{13}$$

In Eq. 6, $Q_{HT,hp}$ and $Q_{HT,he}$ from Eq. 4 and 5 may be used to come to the following definition of ε_{rt} (Eq. 14):

$$\varepsilon_{\mathrm{rt}} = \frac{E_{he}}{E_{hp}} = \eta_{tes} \cdot COP_{hp} \cdot \eta_{he} \tag{14}$$

In the opposite case, i.e. for $\Delta U_{LT} = 0$, the following equation may be written (blue dotted line – Fig. 1) (Eq. 15):

$$\Delta U_{LT} = Q_{LT,he} - \eta_{tes} \cdot Q_{cold,hp} = 0 \tag{15}$$

In Eq. 14, $Q_{LT,he}$ and $Q_{LT,hp}$ from Eq. 4 and 5 may be used to get to the following definition of ε_{rt} (Eq. 16):

$$\varepsilon_{\mathrm{rt}} = \frac{E_{he}}{E_{hp}} = \eta_{tes} \cdot (COP_{hp} - 1) \cdot \frac{\eta_{he}}{1 - \eta_{he}} \tag{16}$$

These equations show that the design specification about where the excess heat should be accumulated affects the system performance. Furthermore, it may be demonstrated how the round-trip efficiency in Eq. 14 is always higher than that in Eq. 16, by plugging the same numerical values into the two equations. This means that accumulating the heat in the LT reservoir should be preferred.

However, some authors choose to do the opposite for practical reasons. In [18], the heat from irreversibility is accumulated in the HT reservoir. This is done because extracting this heat from the HT reservoir may be cheaper and easier, as the heat is stored at high temperatures. As a matter of fact, extracting the heat from the LT reservoir may cost additional work, as an auxiliary heat pump may be needed to move the heat against the thermal gradient between the environment and the LT reservoir. However, this is a strict necessity only in those cases in which the LT reservoir is *entirely* at temperatures lower than the environment, as in [26,27,35]. Often the LT reservoir may be designed in a way that is only partially at temperatures lower than the environment, as in [17,24] and others. In this case, the excess heat may be extracted from the LT reservoir, in the same way as it would be done for the HT reservoir.

Finally, it may be observed how both ε_{rt} definitions must yield $\varepsilon_{rt} = 1$ for ideal systems. In both cases, this happens if the thermal reservoirs are adiabatic ($\eta_{tes} = 1$) and the product $COP_{hp} \cdot \eta_{he} = 1$. This may happen only in the case of perfectly overlapping charge and discharge thermodynamic cycles. This situation may be achieved only in case reversible transformations are performed. This translates into the necessity of having no-heat losses, no-pressure losses and of using isentropic (and adiabatic) machines. In this case, the same thermodynamic cycle may be followed during charge and, in reverse, during discharge, discussed by [18]. In this case, the COP_{hp} and η_{he} are the exact inverse of one another. Thus, their product yields 1.

Several authors [31–35,37,38,41] propose the use of only one heat reservoir. In this case, the choice of which reservoir is emptied to close the charge/discharge cycle is straightforward and the related equation between Eq. 14 and Eq. 16 should be used for ε_{rt}.

Apart from the round-trip efficiency, several other parameters may be used to characterise the CB system, such as energy and power compactness $\gamma_{e/w}$, i.e. energy and power density, measured in kWh/m^3 and kW/m^3. These may be an important criterion to compare different technologies. The definition may consider the energy effectively discharged or charged Eq. 17 and (18):

$$\begin{cases} \gamma_{e,ch} = \dfrac{E_{hp}}{V_{tes}} \\ \gamma_{e,dis} = \dfrac{E_{he}}{V_{tes}} = \dfrac{E_{hp} \cdot \varepsilon_{rt}}{V_{tes}} \end{cases} \tag{17}$$

$$\begin{cases} \gamma_{w,ch} = \dfrac{E_{hp}}{\tau_{ch} \cdot V_{tes}} \\ \gamma_{w,dis} = \dfrac{E_{he}}{\tau_{dis} \cdot V_{tes}} = \dfrac{E_{hp} \cdot \varepsilon_{rt}}{\tau_{dis} \cdot V_{tes}} \end{cases} \tag{18}$$

where V_{tes} is the total TES volume, τ_{ch} is the nominal charge time in h, and τ_{dis} is the nominal discharge time in h. Charge and discharge nominal time are usually derived from electrical profiles, as shown in [17], which suggests that typical required charging times are around 5 h, whereas discharging times are around 3 h.

All the listed indicators do not take into account the possible integration of waste heat. It is not always clear if a thermally integrated Carnot battery is more like a storage of electricity or a waste heat recovery system. Of course, this may depend on the ratio between heat and electric energy input. Furthermore, the direct conversion of waste heat into electricity, for how low the temperature could be, will always be more efficient than any Carnot battery that can be built upon such thermal resources. In [31] it is shown how the ratio between CB's first law total efficiency and that of direct exploitation of the thermal source may range between 1/10 to 1/3, in function of the operating fluids and of the heat source temperature level.

However, the purpose of a CB is to *store* energy, not to produce energy, and this cannot be done without efficiency loss. This is true for all the storage technologies.

While it is true that the first-law efficiency of a thermally integrated CB may be very high, it would be incorrect to consider the heat from the heat source and the electric energy in input as equally valuable. To consider the difference in thermodynamic quality between the two energy streams, a second-law efficiency, i.e. exergy efficiency, may be defined.

If we consider that all the waste heat in input is useful energy, we can define the second law efficiency [57], assuming that all the waste heat energy from high source temperature $T_{in,source}$ to cold source temperature $T_{out,source} = T_0$ could be converted into electricity through an infinite series of infinitesimal Carnot cycles (Eq. 19):

$$\eta_{II,usable} = \frac{E_{he} + Q_{sink}\cdot\left[1 - \frac{T_0}{(T_{sink,max} - T_{sink,min})}\cdot ln\left(\frac{T_{sink,max}}{T_{sink,min}}\right)\right]}{E_{hp} + Q_{source}\cdot\left[1 - \frac{T_0}{(T_{in,source} - T_0)}\cdot ln\left(\frac{T_{in,source}}{T_0}\right)\right]} \tag{19}$$

where Q_{sink} refers to the eventual use of the thermal energy rejected at the condenser of the ORC or of the HP respectively, in the HT configuration (i.e. only HT reservoir), or in the LT configuration (i.e. only LT reservoir). Usually, this thermal energy is wasted, and this term is omitted in standard configurations. $T_{sink,max}$ refers to the high temperature of the sink and $T_{sink,max}$ is the low temperature of the sink.

Another possibility is to consider whether the waste heat not used by the Carnot battery is still useful for additional waste heat recovery systems or for direct use onsite. In this case, only the thermal input effectively used by the Carnot battery is taken into account (Eq. 20).

$$\eta_{II,used} = \frac{E_{he} + Q_{sink}\cdot\left[1 - \frac{T_0}{(T_{sink,max} - T_{sink,min})}\cdot ln\left(\frac{T_{sink,max}}{T_{sink,min}}\right)\right]}{E_{hp} + Q_{source}\cdot\left[1 - \frac{T_0}{(T_{in,source} - T_{out,source})}\cdot ln\left(\frac{T_{out,source}}{T_{in,source}}\right)\right]} \tag{20}$$

An illustration of these performance indicators is shown in Fig. 7. Here, the heat source temperature glide (the difference of temperature between the high temperature and low-temperature storage) used by the Carnot battery is plotted on the x-axis. In this example, the performance indicator of a thermally integrated Carnot battery using an HT storage is shown. In this example, the combination of a CB based on a heat pump and a Rankine cycle is considered with a waste heat temperature of 75°C and an air temperature of 15°C [41].

First, from Fig. 7, the used-to-wasted thermal energy ratio is plotted against the heat source temperature glide. This ratio is defined as the ratio between the heat flow absorbed by the Carnot battery divided by the total available heat flux (from inlet to outlet heat source temperatures). Naturally, this ratio increases with the heat source glide across the Carnot battery. ε_{rt} and $\eta_{II,used}$ decrease with the heat source glide since the mean temperature of the heat source decreases. This has a negative impact on the COP_{hp}, and thus on CB efficiency. However, $\eta_{II,usable}$ increases with the heat source glide until it reaches an optimum. This is because, at low heat source glides, the waste heat recovery is minimal, and most of the heat source potential contribution is wasted. This has a negative impact on $\eta_{II,usable}$ and first law efficiency. On the other hand, i.e. for high heat source glide values, the used-to-wasted thermal energy ratio is high, but the ε_{rt} is low, since it also lowers the COP_{hp} (the heat must be upgraded over a larger heat pump temperature lift).

To conclude this section, Table 2 summarises the different performance indicators.

3. Thermal energy storage

Thermal energy storage (TES) is a crucial component in the overall Carnot battery system. It is positioned between the power-to-heat and the heat-to-power system, and as such its discharge and charging processes need to be adapted to these systems to achieve optimal operation. In this section, different TES technologies are discussed in the scope of Carnot batteries. Benefits and drawbacks are highlighted, and current experimental and theoretical research is summarised. For an in-depth analysis on TES, we refer to the appropriate review papers [58–60].

3.1. Sensible thermal energy storage

For sensible TES (STES) systems, heat is stored or rejected by using an increase or a decrease in temperature, respectively. As such, STES systems use the heat capacity of the filling material to store energy, and the material is always present in a single phase. Typically, this is either the solid or the liquid phase. The most straightforward example of STES with a liquid medium is water, while for a solid medium this would be rock type storage. Both have the advantage of being cheap storage materials. The specific heat capacity of water is roughly four times higher than that of rock type materials. However, water needs high pressures to reach temperatures higher than 100°C, while rock type material can easily go to temperatures of 700°C. A comprehensive list of different materials can be found in several review papers published on the topic [58–60].

It has been noted that, for an STES system, the efficiency strongly depends on the efficiency of insulation provided against thermal leakages. Depending on this, an STES may reach an efficiency as high as 90% and as low as 50% [61]. The authors also highlighted the low specific energy of the STES system of 10 – 50 W_{th}/kg, which leads to a substantial increase in the size of the storage tanks. It has been estimated that the capital costs associated with an STES system are in the range of 3400 – 4500 $/kW [62], while the price per energy unit stored lies in the range of 0.1 – 10 $/kWh [11].

The Brayton Carnot battery is most often based on packed bed sensible heat storage. These use high temperatures, and there is a direct heat transfer with the fluid (e.g. air or an inert gas like argon). Both increase the efficiency of the Brayton Carnot Battery concept. Packed bed dynamic behaviour has been intensely investigated [20,25,56,63] to characterise Brayton PTES transient behaviour, losses, energy density and the relation between efficiency and power output [17,24]. In

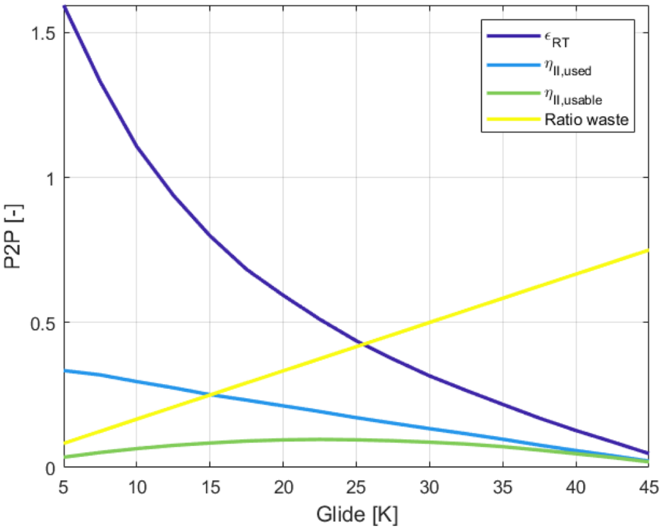

Fig. 7. Performance criteria of a thermally integrated Carnot battery using a HT storage.

Table 2
Summary of performance indicators.

Nomenclature	Full name	units	Equation
ε_{rt}	Roundtrip efficiency	[-]	3
γ_e	Energy density	[Wh/m^3]	17
γ_w	Power density	[W/m^3]	18
η_{II}	Second law efficiency	[-]	19–20

optimised designs, the round-trip efficiency and energy density are less sensitive to losses associated with the packed bed thermal energy storage than to the expander and compressor performance [56]. However, the packed bed also pose challenges, such as high-pressure losses and brittleness due to thermal stresses caused by the cyclic operation. Furthermore, measuring the state of charge in a packed bed is non-trivial and may require direct monitoring of the temperature in several parts of the packed bed. Finally, packed bed thermal behaviour may not allow for an incomplete charge or discharge, and the residual energy may be lost due to internal heat exchange and overall temperature reduction. Some pilot demonstrators are based on molten salt sensible heat storage, to avoid all these issues [16]. A schematic representation of a double reservoir SHTES PTES system is presented in Fig. 8.

3.2. Latent thermal energy storage

For Carnot batteries using latent TES (LTES) systems, heat is stored in materials that undergo a phase change during charging or discharging. The materials used are called phase change materials (PCM). The energy released or absorbed during phase change is known as latent heat, in the context of LTES systems, mostly solid-liquid transitions are taking place [64]. These transitions occur at an approximately constant temperature, hence facilitating the stabilisation of the temperature over which the heat transfer takes place. When heat addition and heat rejection of the energy conversion devices also occur at near isothermal conditions a good match with the LTES can be achieved. As such, irreversibilities associated to finite temperature heat transfer can be reduced.

LTES systems have the advantage of high specific energy (50 – 150 W$_{th}$h/kg) when compared to STES systems; the former can be up to 14 times higher than the latter [62]. However, the capital costs required to establish LTES are in the range of 6000 – 15,000 $/kW and the price per energy unit stored lies in the range of 10 – 50 $/kWh [63], which is significantly higher when compared to STES systems.

Only one prototype of Carnot battery is considering melting of ice as a low-temperature LTES reservoir [40]. As far as the high-temperature reservoir, there are some prototypes under development that make use of molten salts. In project Malta [16], a phase change occurs at high temperature, and the LTES is coupled to a Brayton cycle. Low-temperature storage systems allow for the inclusion of alternative heat streams like waste heat and solar energy, yet, the maximum achievable performance of the heat engine will be lower. The isothermal evaporation and condensation in a Rankine cycle, however, makes a good match with an LTES systems.

Other options include the use of metallic and polymer PCMs. At the moment both are not considered for use in Carnot batteries. Metallic PCMs operate at high temperature and thus could increase the performance of the heat engine. Furthermore, numerical and experimental studies have shown that metallic PCMs are effective in transient high heat flux applications. These applications include the temperature increase in electronic chips [65,66], smartphones [67] and heat transfer in TES systems [68–70]. However, the main drawback is that many metallic PCMs are corrosive, the storage container should be able to sustain this in combination with the high temperature, making this a challenge [71]. Polymers, on the other hand, operate at too low temperatures making them not interesting for use in Carnot batteries.

3.2.1. Liquid air energy storage (LAES)

Although Liquid Air Energy Storage (LAES) has often been considered merely an advancement of CAES [12,72] proposed to improve energy density, LAES is based on different physical principles. As was discussed, LAES stores electrical energy as heat, and not as mechanical energy, hence it should be considered a proper Carnot battery. To store electrical energy, LAES exploits the liquefaction of air, which is a convenient way to store latent heat. Liquefied air is produced cryogenically, at -196°C, which is the boiling point of nitrogen. When LAES is discharged, the liquid air is pumped, heated and expanded in a turbine [12].

Since liquid air is much denser than compressed air, LAES features much higher energy density than CAES [10,72]. Furthermore, the liquid air storage tank is at low pressure, so it is both more compact and cheaper, if compared to that of CAES. For all these reasons, the LAES storage can be directly fabricated. Thus the technology is independent from the pre-existence of caves, mines or other suitable geological formations.

The liquefaction process is the most critical for the LAES operation. Liquefaction can be achieved through a classical vapour compression cycle, through a Linde-Hampson cycle or through more advanced cryogenic cycles.

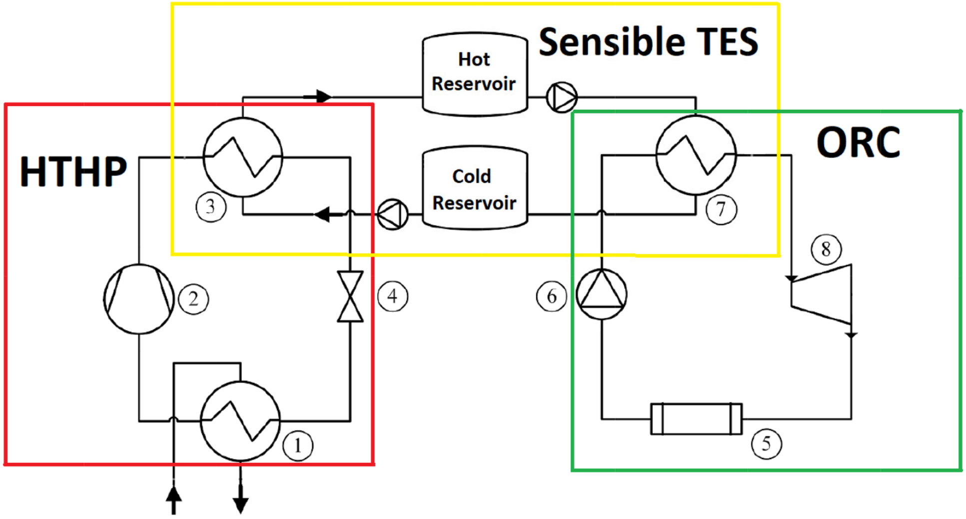

Fig. 8. PTES system with sensible thermal energy storage.

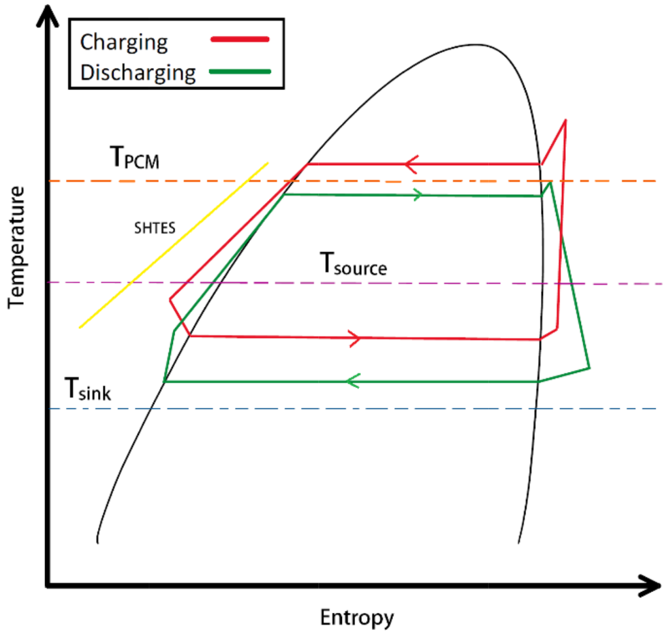

Fig. 9. Charging and discharging cycles in a PTES system employing a sensible and latent heat storage system.

In a Linde cycle, makeup gas mixes with uncondensed gas from the cycle. The mixture is compressed by an ideally isothermal compressor, increasing the pressure of the mixture. The temperature is kept constant by rejecting compression heat to a coolant. The high-pressure gas then enters the heat exchanger where the uncondensed gas cools the gas. At the heat exchanger outlet, the gas is throttled through a valve, expands and its temperature decreases, until condensation occurs. The resulting vapour-liquid mixture enters a phase separator where liquefied gas is obtained [72]. To achieve a higher efficiency, more advanced air liquefaction cycles may be used. Only basic LAES layouts are based on the Linde cycle, which is notoriously inefficient if compared to liquefaction cycles such as Claude and Kapitza [73]. These more advanced configurations are supposed to achieve a higher efficiency [31,74,75].

After the charge phase, there are four main methods of energy extraction from cryogens: the direct expansion method, the Rankine cycle, the Brayton cycle, and a combination of the methods above. Energy recovered from the liquefied air using the Rankine cycle can be as high as 36.8%, while energy recovered from the combined cycle could be increased to 43.3% [72].

To date, only one LAES pilot plant (300 kW, 2.5 MWh) has been successfully commissioned, based on the Claude cycle [76,77]. The plant operates with a round-trip electrical efficiency of around 8%, but the projections for a full-scale facility are up to 50%. The pilot plant was subjected to several dynamic tests to prove its ability to provide ancillary services. The tests were positive, proving the fast response of LAES during discharge.

Apart from using more efficient liquefaction cycles, a very effective technique to improve efficiency is to recycle compression and expansion excess thermal energy in order to use it in the next charge/discharge phase [31]. In LAES, the most considerable exergy loss is the turbine outlet [78]. Therefore, several waste heat recovery solutions were proposed, such as ORC [79–81], Brayton cycle [78] and Absorption cooling [77]. The best strategy, however, could be combining LAES with other systems that could provide the waste heat. For this task, thermal power plants [81], or waste cold from LNG regasification facilities [80,82], have been proposed. In particular, the solutions which exploit the waste cold energy seem to yield the highest efficiencies: 70% [80] and 88% [82] round trip efficiency.

In an attempt to reduce the energy use of liquefaction, alternative fluids like CO_2, which condenses at a much higher temperature than air, have been proposed [12]. Liquefied CO2 energy storage is reported to achieve efficiencies ranging between 40–57% and might have some advantages for the use of more compact equipment [12].

LAES as a technology is considered to be emerging, whereas the essential components for its construction can be considered mature and readily available. Therefore, LAES could be a promising alternative technology for grid-scale storage applications. Thanks to positive features like high energy density and independence from geographical sites, LAES might have some advantages over CAES and PHES. However, LAES generally achieves lower efficiency when compared to these technologies. LAES efficiency could be improved by constructing the LAES facility near to sources of waste heat/cold, such as power plants and LNG regasification facilities. However, this might cause LAES to lose the strategic advantage of being site independent.

3.2.2. *Thermochemical energy storage*

The process of storing and releasing heat through chemical reaction mechanisms is the underlying principle behind thermochemical energy storage (TCES). A chemical material pair can be supplied with heat energy, resulting in their dissociation into individual components that can be separated, thus allowing them to store the provided thermal energy. If these separated individual components react with each other, they associate into a compound, thereby releasing the stored thermal energy.

TCES systems are primarily employed in space heating applications, as solar energy provides a high grade of thermal energy which can be

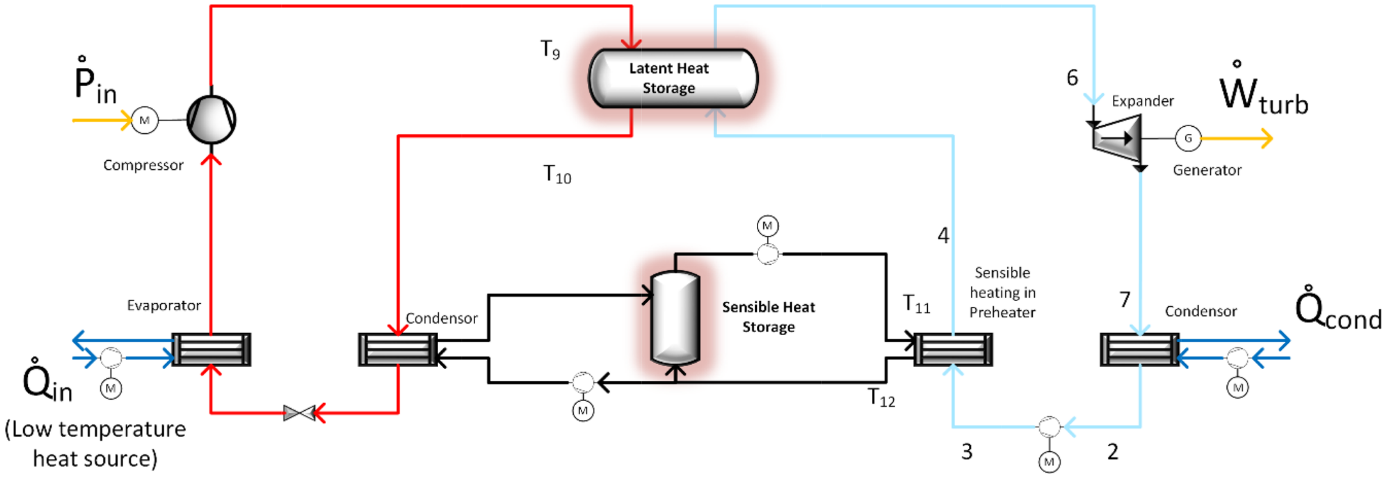

Fig. 10. Pumped thermal energy storage system with a sensible and latent heat thermal energy storage.

utilised effectively in such a system. The capital cost required for a TCES system is the lowest among the three types of storage technologies, and is in the range of 1000 – 3000 \$/kW, and furthermore, the energy density, in the range of 120–250 $W_{th}h/kg$, is the highest. However, the price per energy unit stored is 8–100 \$/kWh, making it the most costly of the three storage technologies [30].

The TCES system possesses advantages when it comes to parameters such as storage capacity and energy density, and it can be stored at atmospheric conditions without losing thermal energy. However, TCES systems are not available on a highly commercial scale, as much research is required to gain a comprehensive understanding of the practical aspects of the technology before commercial implementation can take place [83].

3.2.3. Hybrid thermal energy storage

An emerging method for a large-scale energy storage system combines the latent and sensible thermal energy storage systems. Fig. 9 shows the temperature-entropy plot of such a system, along with a charging cycle involving the ORC and a discharging cycle involving the heat pump. The layout of such a system is visualised in Fig. 10. In [43,63], the authors studied the coupling of low-temperature heat sources with PTES. They developed a numerical model for a subcritical PTES system working with butene. They found that the ratio of supplied electrical power to useful electrical power is 1.25 with a maximum exergetic efficiency of 59%, operating between a source and sink temperature of 100^{0}C and 15^{0}C respectively. If the thermal energy is not utilised, the maximum exergetic efficiency drops to 52%.

It should be noted that the sensible temperature profiles in Fig. 9 are only valid at the beginning of charging and discharging, and that a stratified storage system is assumed. In reality, temperatures will change over time (Fig. 9), leading to a reduced availability to produce work. Thus, even for systems with a good temperature match for the STES, important irreversibilities have to be considered.

3.3. Comparison

Among the three types of TES, many types of configurations and materials are possible. A summary of the main characteristics is proposed in Table 3. More details are given in specific literature [62].

It is interesting to observe which TES is the most suited to the Carnot battery. In the literature, some trends appear, although every combination is theoretically possible:

- For the Brayton Carnot battery and the Rankine cycle using an electrical heater, high-temperature levels are expected. Usually, a packed bed TES consisting of rocks [17] or molten salts [16] are considered. Metallic PCM could also be considered.
- For the Rankine Carnot battery, temperature levels are usually low. Water is generally used due to its low cost and simplicity (for temperatures <150°C). Oil could be used for higher temperatures due to its rather low pressure. PCM are also considered due to their high compactness, but their costs have been limiting their use up to now.
- For applications at temperatures close to 0°C, water can be a very efficient PCM, while at very low temperatures, liquid air is used (-196°C).

4. Industrial state of the art

4.1. Potential impact on the energy market

Emphasis is increasingly being placed on the production of power from renewable energy sources (RES) to decarbonise the electricity sector. Energy storage serves as one of the ways in which this challenge can be tackled. It is estimated that an additional electricity storage capacity of 310 gigawatts that is connected to the grid is required in the United States, Europe, China and India alone [84]. As a means to promote energy storage, governments across Europe, America and Asia are providing support to demonstration projects as an incentive for further growth [85]. The federal government of Germany aims to increase the share of electricity produced by renewable energy to 80% by 2050 [86]. Furthermore, the energy demand is projected to increase in the future. In addition, a very significant degree of decarbonisation is aimed at by 2030. The European Commission suggests a structural change in the process of power generation to renewable energy sources (RES) to achieve 96 to 99% decarbonisation by 2050 [87].

Different countries have different levels of RES penetration in their electricity grid. Curtailment of non-dispatchable RES electricity has been increasingly adopted in these countries in times when electricity production exceeds demand and cannot be transferred elsewhere due to bottlenecks in the electricity grid. Grid extensions are expensive and may not be able to provide a long term solution. This is a significant motivation for transitioning to electrical energy storage (EES) systems [87].

If the envisioned RES integration is to be achieved in the forecasted future, it is necessary to perform a financial and technical evaluation of the currently available EES systems. Most of these studies have been based on the utilisation of well-established technologies such as Pumped Hydroelectric Storage (PHS) and Compressed Air Energy Storage (CAES). It is well understood that PHS and CAES systems are capable of achieving the target costs for ubiquitous applications [84]. However, the inherent restrictions of suitable geographical and geological requirements have pushed the development of alternative electricity storage technologies.

The Carnot battery system is an electricity storage technology that does not face the limitations affecting other competitive technologies. There have been studies evaluating the financial aspects of this technology when compared to other energy storage technologies. Smallbone *et al.* [17] conducted a financial analysis of a Carnot battery system using the Levelised Cost of Storage (LCOS) method and found out that the Carnot battery system can be cost-competitive with the other large-scale storage systems. If there is no cost associated with charging the storage, the LCOS for the Carnot battery system is relatively lower than that of the PHS and CAES system. Benato [88] studied

Table 3
Comparison between the three main types of TES [62].

Type	Power [MW]	Compactness [kWh/t]	Max. Temp. [°C]	Cost [\$/kWh]	Storage period	Typical materials(Max. temp. [°C])
Sensible	0.1–10	10–50	500	0.1–10	Days-months	Water (150) Rocks (900) Oil (350)
Latent	0.001–1	50–150	660	10–50	Hours-months	Ice (0) Molten salt (400) Metallic (500)
Chemical	0.01–1	150–250	180	8–100	Hours-day	NaOH (150) LiCl (100) Zeolite (180)

a packed bed storage Carnot battery system and concluded that the round-trip efficiency achieved was quite poor but could still compete with the PHS and CAES systems against their energy density and specific cost. Another study [89] compared the Carnot battery system with the Liquid-Air Energy Storage (LAES) system. They found out that the Carnot battery system is capable of achieving higher round-trip efficiencies and is competitive when sell-to-buy price ratios are considered, but has a higher capital cost and a higher levelised cost of storage. One study [90] compares the Brayton and Rankine-based Carnot battery system with other grid-scale EES technologies. It was found that, in case of energy arbitrage, if both capital costs and operational expenditures are considered, Carnot battery systems may compensate for their lower efficiency with a very low initial cost. In this way, Carnot battery may potentially outperform more efficient, and costlier, systems such as molten salt batteries and flow batteries.

Although the implementation of EES remains limited at the moment, mainly for financial and technical reasons, it is expected to increase rapidly in the coming years. In this context, an EES technology may be an attractive solution, as it promises to be cost-effective with a long lifetime (unlike many battery chemistries), and site-independent (unlike PHS and CAES).

4.2. *Prototypes under test or construction*

Table 4 presents the different prototypes of Carnot battery that have been developed and were reported in the literature. Since the technology is emerging, many prototypes are being built and this is the reason why this table is also proposed online with continuous updates [91]. Globally, Carnot batteries are not mature yet. Only 2 medium-scale projects have, up to date, been connected to the grid and operated successfully. One of them is a LAES of 300 kW [77]. The second one is an electrical heater combined with a Rankine cycle [50]. However, this system presents a relatively low round-trip efficiency, and other configurations are being investigated. A 150 kW Brayton cycle was successfully tested in 2019 [17]. Furthermore, two thermally integrated reversible HP/RC cycles are being tested on the lab-scale [40,49]. Finally, a 10 kW Carnot battery using a heat pump and a Rankine cycle has been built [92].

It can be noted from this table that only a few configurations have been tested, and intensive experimental research is necessary in order to identify the advantages, constraints and costs for each of them.

4.2.1. *Comparison and discussion*

It is essential to identify which technology of Carnot battery is the most appropriate in a given case study. This task is tricky since this technology is under development and very few prototypes have been built and tested up to now (see Section 3). However, the main characteristics for each technology are summarised in Table 5, with the current state-of-the-art (which could potentially evolve rapidly in the next decade). The five leading technologies are compared: Brayton, a combination of heat pump and Rankine cycle, combination of electrical heater and Rankine cycle, Liquid Air Energy Storage and the Lamm-Honigmann process.

In terms of maximum energy and power, no limit should be taken as a technological constraint since each technology is scalable (up to GW scale).

In terms of temperature, the systems can be divided into two groups: the high-temperature cycles (Brayton and Rankine cycles combined with an electrical heater) and the low-temperature cycles (heat pump combined with a Rankine cycle, Lamm-Honigmann and LAES). Among this latter category, it appears that only the HP/ORC and the Lamm-Honigmann work with a small temperature difference. It means that the thermal integration of waste heat, for example, is more profitable for those two technologies.

The self-discharge depends on the temperature difference between the storage and the ambient. Therefore, it depends on the specific application. Only the Lamm-Honigmann process presents very low self-discharge thanks to its thermochemical reaction.

The price comparison is only qualitative because the numbers provided in Table 5 are expected to evolve in the future. The prices include installation and operational costs. Also, it should be noted that prices depend on the power (and energy) range. In Table 5, prices refer to the power ranges considered for the prototypes in Table 4. From the first economic considerations [17], it appears that the storage would account for a small fraction (8 to 30 %) of the total costs. The electrical heater combined with a RC should be the cheapest if it can re-use existing fossil-fuel power plant. The HP/RC and Lamm-Honigmann cycles should also be cheap since off-the-shelf components are used for the systems but also the thermal energy storage. Finally, the Brayton cycle and LAES seem to present similar costs according to the literature.

Up to now, the technological maturity of an electrical heater combined with RC and LAES is already proven (Table 4). Carnot Batteries based on HP/RC cycles are not as mature as the two aforementioned technologies, but the heat pump and RC are already developed worldwide, and some large-scale demonstrators should be built in the coming years (see Table 4). The Lamm-Honingmann process is not mature since only one demonstrator is found in the literature (Table 4).

The Lamm-Honigmann process presents the lowest round-trip efficiency (ε_{rt}), but the latter could probably be improved significantly since this technology is arguably the least mature. The electrical and RC technology presents the second-lowest ε_{rt} because of the low performance of an electric heater compared to a thermodynamic cycle. The highest ε_{rt} are obtained with the Brayton cycle and the HP/RC (particularly with thermal integration). The ε_{rt} of the LAES is lower than the two aforementioned cycles.

The Rankine PTES could be a valid alternative to Brayton because it generally achieves higher energy densities and it stores energy at much lower temperatures, which is beneficial for thermal losses and the choice of reservoir/machines materials. Furthermore, it may allow for the use of phase change materials as a storage medium.

A comparison of the Carnot battery with other electrical storage solutions lies outside the scope of this paper. However, the reader can

Table 4
Carnot battery existing prototypes.

Year	Type	Electrical power [kW]	Electrical energy [kWh]	Working fluid	Storage	Temp. [°C]	ε_{RT} [%]	Refs
2019	TI Inv. rev. HP/ORC	2	-	R1234yf	Ice (1m^3)	60	100	[40]
2019	TI Inv. Rev. HP/ORC	1	10	R1233zd	Water (1m^3)	90	100	[49]
2014	Electrical heater + Rankine	700	5 000	Water	Rock (40 t)	600	45	[50]
2019	Electrical heater + Rankine	1400	12 000	Water	Rock (1000 t)	600	45	[50]
2019	Brayton	150	600	Air	Packed bed (9m^3)	500	72	[17]
2019	ORC + HP	1000	-	R1233zd	Sensible + latent	180	-	[92]
2011	LAES	300	2500	Air	Air	-	12	[76]
2018	LAES	5000	15,000	Air	Air	-	-	[77]
2020	Rev. HP/ORC	7500	250,000	CO2	Water	150	-	[93]

Table 5
Comparison of the different technologies.

Cycle	Brayton cycle	Electrical heater and Rankine Cycle	Heat pump and Rankine cycle	Liquid Air	Lamm-Honigmann
Power [MW]	Up to 100	Up to 100	Up to 10*	[10–7800]	N/A
Energy [MWh]	Up to 400	Up to 400	Up to 40*	[50–650]	N/A
Temp. [°C]	[-70:1000]	Up to 750	Up to 150	-196	N/A
Compactness [kW/m^3]	25	~4	[0.05–1.72]	[6–46]	N/A
Compactness [kWh/m^3]	200	~36	[0.2–207]	[32–230]	N/A
Self-discharge	medium	Very low			
ε_{rt} [%]	[60–70]	[12–55]	[30–73] [70–150]**	[12–60]	[4- N/A]
Price [$/kW]	[395–875]	~376	[272–468]	[329–3846]	N/A
Price [$/kWh]	[55–198]	~94	[68–117]	[66–666]	N/A
Estimated TRL	5	9	7	9	1
Typical fluids	Argon, Air	Water	R1233zd(E),CO2, NH3, water	Air	H_2O/LiBr, H_2O/NaOH
References	[17,25]	[50]	[38,92]	[82]	[53]

* Possible to extend the range by association in series.

** Thermally integrated.

consult other references [38,55].

5. Conclusions

This review of the Carnot battery technology proposes a state-of-the-art of this very innovative technology. First, a standard definition is proposed to identify which technologies are to be included.

In this paper, Rankine, Brayton, LAES and Lamm-Honigmann Carnot batteries are considered. Each of them is described, and the possible layouts are compared. Furthermore, a review of the Thermal Energy Storages is proposed and shows which technology should be used with each application.

In addition, new performance indicators are proposed as a standard to define the performance of the technology.

Finally, existing prototypes and orders of magnitudes of compactness, performance, range of power and maturity for the different technologies are given. Based on this background, guidelines are drawn to select the optimal configuration for a given case study.

6. Perspectives

As already mentioned, the Carnot battery technology is relatively recent, and many aspects have to be studied in details. Here is a list with the main challenges to overcome to obtain a complete characterisation of the Carnot batteries.

- Part load performance. Many technologies are in a stage that only thermodynamic design has been proposed, so part load calculations should be addressed to provide operators with an idea of how much performance degrades in part-load operation. This is especially interesting since part load also means changing working temperatures. This leads to severe issues as the TES temperatures link the charge and discharge, so a part load in one of the phases might also influence the other subsequent phase.
- Dynamic simulations. Storage sytems must be able to respond quickly. Currently, it is not clear what are the characteristic start-up times of the different CB technologies. Start-up times should be provided for so-called hot start, warm start and cold start conditions. This would characterise the CB in a similar way to thermal power plants. Furthermore, such a dynamic analysis would clarify whether CB can be considered flexible enough to provide the grid services required for the RES integration and on which time scale. For example, can a CB provide frequency regulation, or is it useful only for shifting large quantities of energy from a moment of the day to another?
- Machine selection and design in Brayton PTES. Preliminary studies demonstrated that polytropic efficiency of the cycle components must be very high (> 0.9) to achieve acceptable round-trip efficiencies. However, both working fluid (argon) and inlet /outlet machine conditions are non-standard. Furthermore, in the charging phase, Brayton PTES operates with compression at a very high temperature, as the transformation starts at 350 °C – 400 °C and may theoretically end at 1000 °C. Such operating conditions are currently unfeasible, as modern gas turbine compressor can only operate up to 500 °C. For the listed reasons, the research should focus on the characterisation and design of the machines required for such systems.
- Integration with other systems. PTES round-trip efficiencies should be improved to reduce the losses that a CB battery in mass deployment would cause to the electrical systems. In particular, thermally integrated systems prove to have substantial advantages in terms of electric energy loss reduction. However, only a few studies investigated the TI-PTES integration in terms of the actual availability of waste heat/cold energy streams to exploit. In other words, where, how often and at which cost additional thermal energy streams are available? What is their power? Since the available heat flow is fixed by the upstream system (e.g. an industrial facility, for waste heat), how big the electrical storage system can be, given the available waste energy? Lastly, given the answer to the questions above, what is the real technical potential for TI-PTES systems?
- Experimental validation of theoretical studies. As the PTES technology is very novel and many technological breakthroughs are expected in the next decade, experimental validation of each concept and architecture is crucial to identify which system present the optimal combination of features depending on the case (power/capacity range, additional thermal energy availability, etc.).
- Carnot battery control. Control strategies should be developed and studied to maximise the selected objective function, depending on the chosen CB concept, its power/capacity range, the electricity price fluctuations, the electrical demand and production and the eventual integration of waste heat.
- Finally, it would be very helpful to provide an accurate and validated cost estimation for each type of CB. This would actively help to promote the PTES technology and to obtain the trust of investors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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