



Review

# A Review of Thermochemical Energy Storage Systems for Power Grid Support

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**Abstract:** Power systems in the future are expected to be characterized by an increasing penetration of renewable energy sources systems. To achieve the ambitious goals of the "clean energy transition", energy storage is a key factor, needed in power system design and operation as well as power-to-heat, allowing more flexibility linking the power networks and the heating/cooling demands. Thermochemical systems coupled to power-to-heat are receiving an increasing attention due to their better performance in comparison with sensible and latent heat storage technologies, in particular, in terms of storage time dynamics and energy density. In this work, a comprehensive review of the state of art of theoretical, experimental and numerical studies available in literature on thermochemical thermal energy storage systems and their use in power-to-heat applications is presented with a focus on applications with renewable energy sources. The paper shows that a series of advantages such as additional flexibility, load management, power quality, continuous power supply and a better use of variable renewable energy sources could be crucial elements to increase the commercial profitability of these storage systems. Moreover, specific challenges, i.e., life span and stability of storage material and high cost of power-to-heat/thermochemical systems must be taken in consideration to increase the technology readiness level of this emerging concept of energy systems integration.

Keywords: thermochemical storage; sorption heat storage; power-to-heat; power grid support

## 1. Introduction

Decarbonization of the power sector, increase of energy efficiency and energy security are the major focus of several policies to achieve ambitious climate targets in the next years [1,2]. In the evolution of the energy systems, renewable energy sources (RES) play a major role towards the achievement of environmental sustainability [3–5]. Due to their stochastic nature, however, renewable energies are not programmable so their energy generation is usually not adjusted in order to match electricity demands [6,7]. To guarantee the stability of the power grids, the instant balance of temporal and spatial mismatch between generation and loads can be achieved introducing flexible elements in the power networks [8–13]. Flexibility is defined as the capability to balance rapid changes in power generation according to Bertsch et al. [14] or variation and uncertainty in net load according to Denholm et al. [15]. Several definitions of flexibility can be found in the literature [15–18].

Power-to-heat (PtH), based on the conversion of electricity into heat and its reverse process Heat-to-Power (HtP), are well recognized processes among the most mature demand-side management (DSM) options [19–21].

Appl. Sci. 2020, 10, 3142 2 of 35

These techniques are particularly promising to provide renewable energy integration, power grid flexibility [12,13,22,23] and power sector decarbonization contributing to a better utilization of existing assets supporting the RES penetration into the electricity supply mix [24–29].

Thermal energy storage systems (TESs) can be effective in improving the mismatch between energy generation and use in terms of time, temperature, power or site leading to an increase of the overall efficiency and reliability [30–34]. Reduced investment and running costs, lower pollution and less greenhouse gases (GHG) emissions are some of the advantages connected to the use of these technologies [35,36] including: sensible, latent and thermochemical storage [37–41].

Coupling thermal energy storage to a PtH technology to provide flexibility to the power system is a promising option of the demand-side management strategies currently investigated [42,43]. In particular, turning surplus of variable renewable electricity (VRE) into heat to be stored as thermal energy offers a significant additional flexibility with a great potential in stabilizing the grid voltage [42,44]. In particular, during off-peak times, heating or cooling can be generated by thermal energy and then used during peak-hours flattening the customer's load profile [45]. In this way, customers can have a more efficient system and also be cost-efficient. They can take advantage of different electricity prices during peak and off-peak hours and for utilities that can spread the demand over the whole day [46,47].

Several studies examine the coupling of thermal storage with power-to-heat systems (PtHs) for several purposes, e.g., buffering, heating and cooling, transport of residual heat [48–50]. In general, small-scale PtH and TES applications can be applied in the residential and commercial sectors while large scale are mainly focus on industrial applications such as district heating grids [51,52].

Storage devices have great advantages not only in terms of flexibility of the entire power system [53,54] but also in terms of economic profitability with higher efficiency and cost effectiveness of the power grid as shown in the studies of Christidis et al. [55] and Jamshid et al. [56]. In a recent study (2020) Meroueh and Chen [57] provided a detailed analysis on the potential from TESs to provide a cost-effective solution for grid level integration in the near term for renewable-based plants. Several studies show the potential of heat pumps and thermal energy storages in terms of load shifting, energy consumption and increasing self-sufficiency [58–62].

This work is focused on thermochemical thermal energy storage (TCTES) systems coupled with PtH technologies. In particular, the aim is to provide a comprehensive review on the state of art of thermochemical thermal energy storage systems (TCTESs) and their applications in PtH technologies, including theoretical, experimental and numerical studies. Recent advancements and their potential perspectives will be discussed.

This review is structured as follows. In Section 2 a classification of storage system is reported. Section 3 is a review of the state of art of both sorption and chemical reaction TCES processes and the related main operation processes. Section 4 includes a general description of PtH technologies and an analysis of recent case studies on the application of TCTES systems. Section 5 presents the conclusions of this paper.

## Power-to-Heat Technologies: Classification

Power-to-heat (PtH) is the classification including all devices that perform the conversion of electricity into heat. It is one of the most relevant flexibility options of the DSM [63,64]. With the aim to ensure the integration of the renewables, PtH technologies (PtHs) are considered crucial sources of system flexibility [65]. PtHs contribute to both a better utilization of existing assets and use of temporary renewable surplus generation [65]. When there is an excess of generation, electricity is converted into heat, in this way, additional power in the situations of increased load, is provided contributing, in the same time, to peak shaving, load shifting and energy conservation [66]. Turning surplus of electricity into heat, including thermal energy storage, offers a significant additional flexibility with a great potential in stabilizing the power grid [67,68]. The conversion into thermal energy can be performed through centralized and decentralized options. According to Olsthoorn et al. [69] in the centralized option the electricity is converted into heat at a location far from the point of actual heat demand. By

Appl. Sci. 2020, 10, 3142 3 of 35

district heating systems (DHS) heat is distributed through pipelines to its use. In contrast, according to Lund et al. [70] in the decentralized approach the conversion is in a point right or very close the location of heat demand. Heat is distributed without districting networks. A schematic example of the power-to-heat concept is shown in Figure 1:

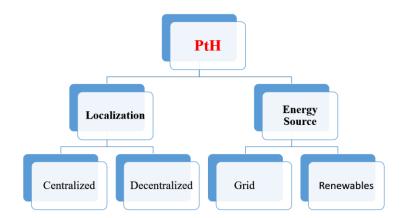


Figure 1. Schematic concept of power-to-heat technologies.

DHS are considered particularly promising due to several advantages in energy production, distribution and consumption, especially for space heating applications [71,72]. In particular, the systems using RES have the advantage that renewable technologies can be placed on the energy supplier side in the actual distribution network or be installed on individual buildings [73–75]. In literature, district heating networks are commonly described as one of the most effective solution towards a low-carbon feature [76–81]. Lund et al. [12] in a review of nearly four hundred studies on energy flexibility showed that the interaction between the electricity and district heating sectors is a promising option for increasing energy system flexibility. Heat pumps (HPs) and resistive heaters are the main centralized technologies to draw electricity from the grid to generate heat to be connected to the thermal storage [73].

According to Lund et al. [70] in the decentralized approach the conversion occurs at a site very close to the location of heat demand without networks, grids and piping. The decentralized technologies have several advantages in energy production, distribution and consumption, in particular, providing a sustainable, economical and future-proof solution for heating large spaces [82,83]. A common classification of the decentralized options is among technologies combined with thermal energy, referred as thermal energy storage coupled heating, and technologies without energy storage, referred as direct heating [26]. Heat pumps, resistive boilers, smart electric thermal storage, fans, radiators are examples of the more widely used decentralized power-to-heat technologies [63,84–87]. Electric boilers are the cheapest alternative due to their low investment costs and can be switched on and off at low cost [88]. HPs enable flexibility in smart grid operations [59,85,89]. However, HPs usually function as a base load technology due to their higher efficiencies [90–92]. To further reduce energy use during operation, waste heat from industrial processes or renewable heat sources can be used as heat source with the advantage that they are not dependent from weather conditions and temperature fluctuations, like for example solar and ground sources. In this way heat generation is more stable and better suited as input for HPs [93,94].

HPs used for power-to-heat applications are electrically driven because electricity is used to lift low exergetic heat to a higher temperature and consequently higher exergy level by running a vapor compression cycle [89,95,96]. Electricity renewable is an option to reduce the use of fossil fuel [97,98]. During periods of low demand and high renewable energy generation, the excess of electricity can be converted into heat and stored in TESs [99]. In contrast, the stored energy is released when demand is high and renewable power production is low [100–102]. In this way, HPs contribute to peak shaving, load shifting and energy conservation with benefits not only to the decarbonizing of

Appl. Sci. 2020, 10, 3142 4 of 35

the heating sector but also in the improving the capacity utilization of renewable power generation infrastructures [87,103]. In literature several examples of heat pumps coupled to TES systems, mainly sensible storage systems, are proposed [104–108]. These devices can both provide flexibility to the power system and increase the use of electricity from renewables plants [108–110]. The capacity of the thermal storage is limited by the maximum condenser temperature of the heat pump coupled. Thus, the maximum state of charge is attained when a predefined temperature in the storage is reached [87].

## 2. Classification of Thermal Storage Systems

Storage technologies can be classified with respect to underlining heat storage principle into: sensible, latent and thermochemical [82,111].

Sensible thermal energy storage (STES) is based on storing thermal energy by cooling or heating of a liquid/solid storage medium. Sensible heat determines a temperature linear change (increase or decrease) in the thermal storage material, without changing its chemical composition or phase. Sensible heat  $Q_s$  depends on the temperature change and the specific heat capacity of the storage material. The amount of energy stored (J) is as followed (1):

$$Q_s = mc_p \Delta T \tag{1}$$

where:

- *m* is the mass of the storage medium (kg);
- $c_p$  is the heat capacity of the storage medium (J/(kg K));
- $\Delta T$  is the temperature difference (°C).

It is important for sensible heat storage systems to use a heat storage material having high specific heat, good thermal conductivity, long-term stability under thermal cycling, compatibility with its containment, recyclability, a low  $CO_2$  footprint and low cost [112]. Sensible heat storage is most widely used in building applications [30].

Latent thermal energy storage (LTES) is based on storing heat into a storage medium undergoing a phase transition [113]. Thermal storage materials store their latent heat during phase change from solid to liquid. The latent heat is stored without a temperature change. The amount of energy stored (J) is as followed (2):

$$Q_l = m\Delta h \tag{2}$$

where:

•  $\Delta h$  is the melting or phase change enthalpy (J/kg).

Micro-encapsulated paraffin based phase change materials PCMs or water-based ice-storage are among methods most suitable can be used [114].

Thermochemical or sorption thermal energy storage (TCTES) recovers the reaction enthalpy involved in a reversible chemical/adsorption reaction [115]. According to Scapino et al. [36] the chemical reaction takes place between a sorbent, which is typically a liquid or solid, and a sorbate, which is, e.g., a vapor. During the charging process, a heat source is used to induce an endothermic reaction, the sorbent and sorbate are separated. The chemical/physical energy of the two components can then be stored separately. During the discharging process, an exothermic reaction occurs and heat stored is recovered.

Characteristics of Thermal Storage Systems

The following features can be used to characterize an energy storage system [21,116,117]:

Storage period defines how long the energy is stored (i.e., hours, days, weeks);

Appl. Sci. 2020, 10, 3142 5 of 35

Power defines how fast the energy stored in the system can be charged and discharged. In
particular, power capacity (W) is the maximum amount of power that can be delivered by the
storage system during discharging while Power density (W/l) is the ratio between the power
capacity and the capacity of the energy storage system;

- Energy storage capacity or energy capacity is defined as the amount of energy absorbed in the storage system during the charging process under nominal conditions. The quantity of stored energy in the system after it is charged depends on the storage process, storage medium and size of the system;
- Energy density or volumetric heat capacity is defined as the ratio between the stored energy and the volume of the energy storage system;
- Charge and discharge time defines how much time is needed to charge or discharge the system.
   The maximum number of charge-discharge cycles in the specified conditions is defined as the cycling capacity or number of cycles;
- Self-discharge is the amount of energy initially stored and dissipated over a specified non-use time;
- Efficiency is the ratio of the energy provided to the user to the energy needed to charge the storage system. It accounts for the energy losses during the storage period and the charge/discharge cycle;
- Response time is defined as the speed with which the energy is absorbed or released [h];
- Cycle life refers to how many times the storage system releases the energy after each recharge;
- Costs are indicators to define the overall cost normalized on the total amount of capacity (€/kWh) or power (€/kW). They are capital costs, and operation and maintenance costs of the storage equipment during its lifetime;
- Cost per output (useful) energy is the ratio of the cost per unit energy divided by the storage efficiency;
- Cost per cycle is defined as the cost per unit energy divided by the cycle life.

Typical values of the above-cited parameters for thermal energy storage technologies are reported in Table 1. With respect to the storage period, TES methods are referred as short-term when heat input and output occur within an interval of several hours or days and, instead, as long-term if the time frame is within an interval of few months or even a whole season [118]. In contrast to STES and LTES, TCTES are particularly suitable for long term storage [119]. The reason is that during the storage phase there are no significant energy losses (no self-discharge) [23]. STES and LTES require insulation systems during storage and thus, to avoid thermal losses, heat cannot be stored for a long time [21]. Despite its seasonal storage potential, TCTES for hot/cold demand is still in early development with few prototype set-ups [120].

Storage energy density is a crucial factor to select a thermal energy storage system for a particular application [121]. Because of its potentially higher energy storage density—5 to 10 times higher than latent heat storage system and sensible heat storage system respectively [112]—TCTES is receiving an increasing attention in several domains [122]. High energy density makes thermochemical thermal energy storage systems (TCTESs) such more compact energy systems so their use, reducing the volume of the system, could be very effective in the situations whereas space constraints are significant [123].

**Table 1.** Parameters of thermal energy storage systems (TESs) [122,123].

TES System	Capacity (kWh/t)	Power (MW)	Efficiency (%)	Storage Period	Cost (€/kWh)
Sensible	10–50	0.001-10.0	50-90	days/months	0.1–10
Latent	50-100	0.001-1.0	75–90	hours/months	10-50
Thermochemical	120–250	0.01-1.0	75–100	hours/days	8–100

A further simplified economic comparison shows that STES is less expensive than LTES and TCTES. High capital costs are among disadvantages that make TCTESs not widely available in the market [119].

Appl. Sci. 2020, 10, 3142 6 of 35

#### 3. Thermochemical Heat Storage: Description of Materials and Processes

A schematic classification of thermochemical heat storage principles is shown in Figure 2. With respect to type of reaction, thermochemical processes are divided into reversible chemical reactions and sorption processes [124]. The fixation or capture of a gas or a vapor by a sorbent is referred as sorption (adsorption and absorption) [125]. In contrast, chemical reactions (solid–gas, solid–liquid) are characterized by a change in the molecular configuration of the compound involved [125].

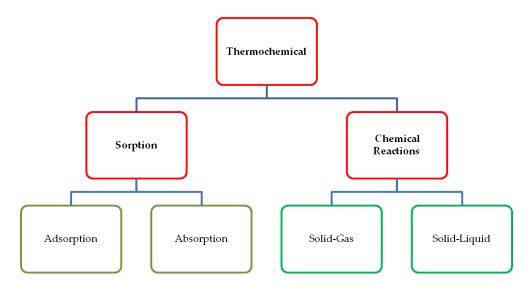


Figure 2. Thermochemical Heat Storage principles classification.

Some authors, e.g., Yu et al. [126], use the definition sorption storage to indicate both reversible chemical reactions and sorption processes.

The thermochemical process consists of desorption, storage and sorption [127]. Desorption is the charging process during which heat, supplied to the storage material, is stored in the form of chemical potential by breaking the binders between the sorbent and the sorbate [128]. Storage is the phase in which the sorbent and the sorbate are separated [129]. Sorption is the discharging process aimed at recovering heat by contacting the sorbent and the sorbate [130].

For desorbing the storage material, any system can be used as heat source. Solar energy [131–133] or micro combined heat and power (CHP) [134,135] are examples of heat sources.

As an example, Lass-Seyoum et al. [136] used industrial waste heat and heat from CHP systems, Helden et al. [137] thermal collectors, Zondag H. et al. [138] exhaust air from buildings. Li et al. [139] developed a thermochemical (sorption) storage system based on use of methanol to recover the heat from photovoltaic (PV) panels.

#### 3.1. Thermochemical Processes and Materials

According to Y. Ding [125], sorption is the phenomenon of fixation or capture of a gas or a vapor by a substance in a condensed state. As shown in Figure 2, sorption processes are classified into absorption and adsorption [140]. According to Nic et al. [141] absorption is defined as "the process of one material (absorbate) being retained by another (absorbent)". According to Yu et al. [126], adsorption is defined as "a phenomenon occurring at the interface between two phases, in which cohesive forces act between the molecules of all substances irrespective of their state of aggregation". An important difference is that absorption occurs at the sorbent molecular level by altering its composition and morphological structure, adsorption occurs at the surface of the adsorbent [34,142]. As shown in Figure 2, solid/gas and liquid/gas systems are example of working pairs used for sorption processes.

These processes are used to store both low-grade heat (<100 °C) and medium-grade heat (100-400 °C) [143-145]. High kinetics at low temperatures make the sorption processes particularly

Appl. Sci. 2020, 10, 3142 7 of 35

attractive for low-temperature applications such as space heating, domestic hot water preparation or other low-grade and medium-grade heat uses [7,146–152]. Usually sorption materials are liquid, solid and composite sorbents [35,153]. Example of working pairs are:

- LiBr solution/H<sub>2</sub>O [154,155];
- LiCl solution/H<sub>2</sub>O [156–158];
- LiCl/activated alumina [159,160];
- LiCl/expanded graphite [161];
- LiCl<sub>2</sub> solution/H<sub>2</sub>O [162];
- CaCl<sub>2</sub> solution/H<sub>2</sub>O [163–165];
- Binary sales [166–174];
- Zeolite 13X [175–182], Zeolite 4A [183–189], Zeolite 5A [190,191];
- Aluminophosphates (ALPOs) [192] and Silico-aluminophosphates (SAPOs) [193–195];
- Composite materials made up by the combination of a salt hydrate and an additive with a porous structure and high thermal conductivity (expanded graphite [196,197], metal foam [198], carbon fiber [199] and activated carbon [199]).

(ALPOs) and (SAPOs) are among promising examples of sorption materials, in particular, for low temperature heat storage [200,201]. Among zeolites, Zeolite 13X is one of the most common thermochemical material in current research due to its hydrothermal and mechanical stability and corrosion behavior [190]. Example of composite materials are CaCl<sub>2</sub>-Silica gel/H<sub>2</sub>O [202], CaCl<sub>2</sub>-FeKIL<sub>2</sub>/H<sub>2</sub>O [203,204], LiBr-Silica gel/H<sub>2</sub>O [205], MgSO<sub>4</sub>-Zeolite/H<sub>2</sub>O [206,207], MgSO<sub>4</sub>-MgCl<sub>2</sub>-/H<sub>2</sub>O [208,209].

Chemical reactions are used to store medium (100–400  $^{\circ}$ C) and high (>400  $^{\circ}$ C) grade heat [210–212]. Example of chemical reactions are:

- dehydration of metal hydroxides [213–218];
- dehydration of metal hydrides [219–224];
- dehydration of salt hydrates [151,225–230];
- deammoniation of ammonium chlorides [172,231–233];
- decarboxylation of metal carbonates [121,234–239];
- methane steam reforming [240–242];
- catalytic dissociation [243–245];
- metal oxide redox [246–248].

The interest towards dehydration of metal hydroxides is not recent, e.g., the hydration of MgO has been extensively studied as early as 1960 [249,250], the dehydration of  $Ca(OH)_2$  has found wide attention as early as 1988. In particular, under support of the National Energy Administration, the American Pacific Northwest National Laboratory started the research on  $Ca(OH)_2/CaO$  as energy storage system [251]. In this context, Liu et al. [251] developed an experimental set up to investigate thermal cycling stability of the  $Ca(OH)_2/CaO$  system laying the foundation of applying this system to practical. A similar experimental set up was developed by Schaube et al. [252].

 $Ca(OH)_2/CaO$  is among more used systems in chemical processes [253–256]. This system has numerous advantages, e.g., efficient reaction kinetics [257] and high reaction enthalpy (104.4 KJ/mol) [258]. It is a very suitable material in thermal storage systems [259], in particular for high-temperatures (400–600 °C) applications [260]. In the context of power-to-heat applications the usage of  $Ca(OH)_2/CaO$  thermochemical systems coupled to heat pumps is arousing great investigation with a particular focus on heat and mass transfer process [261–263].

Also the interest towards metal hydrides is not recent, these thermochemical storage systems were explored since the mid-1970s [264]. Several applications and different metal hydrides systems were explored for thermochemical heat storage [265–269]. Among metal hydrides, Mg-based systems

Appl. Sci. 2020, 10, 3142 8 of 35

are promising as thermochemical storage materials owing to high reaction enthalpy as shown in the studies of Gigantino et al. [223] and Shkatulov et al. [53]. Mg-based metal systems show cyclic stability over a temperature range from 250 °C to 550 °C in which high thermal energy densities of up to 2257 kJ/kg are reached [130]. The abundance of metal hydrides, low cost, high reaction enthalpy, high storage density are among characteristics attracting extensive investigations [219]. These systems, are suitable for both low and high temperature applications [270]. As an example, Sheppard et al. [270] investigated the potential of metal hydrides for low temperature applications while Ronnebro et al. [220] investigated their use for high temperatures applications, in particular based on experimental and modelling results they designed and fabricated a prototype to store both hydrogen and heat with solar technologies. In accordance to other studies, they showed that metal hydrides show both good reversibility and cycling stability combined with high enthalpies. A study about the future perspectives of thermochemical storage based on use of metal hydrides for solar technologies have been developed by Manickam et al. [271].

High energy density and desorption temperatures make salt hydrates fitting with the use of power-to-heat technologies, waste heat sources, solar thermal collectors, particularly investigated and proposed for seasonal heat storage of solar energy in the built environment [150,272,273]. N'Tsoukope et al. [274] investigated 125 salt hydrates for low temperatures heat storage and found that SrBr<sub>2</sub>·6H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O are among the most promising choices for thermochemical storage applications. To investigate the potential energy storage density and the storage efficiency of salt hydrates, a micro-combined heat and power system was developed for the storage of heat generated. They found that for applications requiring lower discharging temperatures like 35 °C, the expectable efficiency and net energy storage density was low. Their results are in accordance to [275–279]. Salt hydrates are considered the most suitable materials for residential applications owing to their high energy density (400-870 kWh·m<sup>-3</sup>) and low turning temperature [280].

Metal carbonates have several advantages, e.g., high energy density, nontoxicity, low costs and widespread availability. All these properties make them suitable for thermochemical storage applications [281–284]. Among suitable alternatives, the combined use of CaO/CaCO<sub>3</sub> (density 0.49 kWh/kg), proposed by Barker in 1973 [283], is largely investigated. In a recent study Fernandez et al. [235] used the working pair CaO/CaCO<sub>3</sub> to develop a system referred as Photovoltaic-Calcium looping (PV-CaL) as large scale storage system. They showed that the high turning temperatures of the exothermic carbonation reaction allows using high-efficiency power cycles. CaCO<sub>3</sub> is one of the most abundant materials in nature. Its use circumventing the risk of resource scarcity may not compromise the economic and technical viability of a thermochemical storage system [236].

The performances of a storage system based on chemical reactions or sorption processes are strongly dependent on the nature of the storage material chosen [125,285,286]. High heat storage capacity and good heat transfer are important characteristics affecting the performance of the heat storage systems. In the choice of the storage materials, parameters such as the cost, environmental impact, and safety conditions should be also taken into account [54,287,288]. Despite many materials being widely investigated, research is always under development to increase material performance with respect to storage density and heat transfer properties [288,289].

Note that among the various thermochemical storage materials described in this section, only few of them have been used so far in power-to-heat applications, as will be shown in more detail in Section 4.1.

# 3.2. Thermochemical Heat Storage Systems

Thermochemical heat storage systems with respect to system configuration can be divided in open and closed systems [274,290,291]. Open systems work at atmospheric pressure in contact with the environment while closed ones work with pure vapor, circulating in hermetically closed loops, at vacuum pressure [292]. A schematic sketch of a closed and open system is shown in Figure 3.

Appl. Sci. 2020, 10, 3142 9 of 35

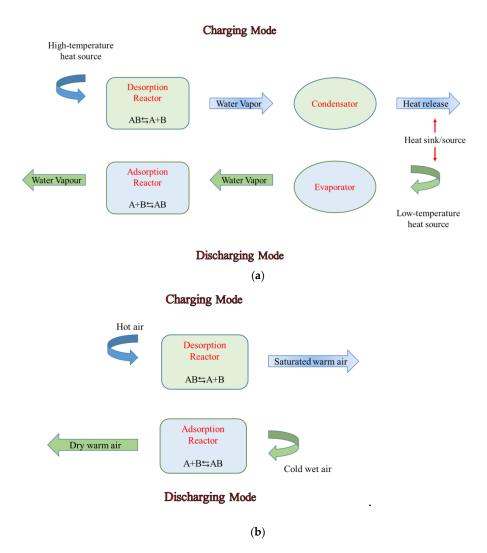


Figure 3. Schematic sketch of (a) closed and (b) open thermochemical system.

A closed system is usually based on a sorption reactor (heat exchanger), a condenser and an evaporator. During the charge process (desorption), heat must be supplied to the storage material at high temperature in the sorption reactor. Desorbed water vapor, released from the sorbent, is condensed at low temperature. The liquid is stored in the reservoir while the heat of condensation can be used either as a low-temperature source or rejected to the environment. After the accomplishment of the charging mode, the storage materials and components will cool down to ambient temperature so during storage no further energy losses occurs. When heat is needed, the valve between the evaporator and sorption reactor is turned on and discharging mode occurs. During the discharging process (adsorption), heat is supplied to the liquid stored in the evaporator at low temperature; the resulting steam is adsorbed in the adsorber releasing heat. Adsorption is a completely reversible process so heat supplied for desorption is equal to the heat gained back during adsorption. Liu et al. [156] developed a seasonal storage system and evaluated that the storage capacity increases with the evaporator temperature and decreases with desorption temperature.

As shown in Figure 3b an open system is less complex in its design. It can be directly connected to the ambient air where the moisture for sorption process is obtained; there are no evaporator or condenser. During the charging mode hot air flows into the sorption reactor releasing water vapor into the air itself. Output is saturated warm air. When heat is needed, cold wet air from the environment is blown into the sorption reactor. Open systems are usually equipped with one or more fans to ensure the ambient air flow into the sorption reactor [129].

The key component of the above described systems is the thermochemical reactor. The reactor can be integrated [293] or separated [294]. In an integrated reactor, the material is stored in the tank where it reacts, while the chamber where the reaction takes place is separated from the thermochemical material storage tank. In a separate reactor the dissociation between the thermal power and the installation storage capacity increases the storage density of the process since there is no need for vapor diffusers and heat exchangers are integrated into the reactor. Moreover, this kind of reactor can also work in steady-state conditions, providing a constant thermal power output [295].

Energy and exergy methods to assess the performances of closed and open systems have been carried by Abedin and Rosen [294]. The authors compared open and closed systems based on use of zeolites 13X. 50% and 9% are the values obtained for energy and exergy efficiency, respectively, in closed systems, 69% and 23% in open ones. Since the exergy efficiencies of both systems are lower than the energy efficiencies it means that there is a margin for loss reduction and efficiency for TCTESs [119]. From a numerical comparison between the two designs, Michel et al. [290] concluded that heat transfer is the main limitation in closed systems while it is mass transfer (vapor transfer to the adsorbent during discharging) in open ones.

Many prototypes of both type of systems have been developed. One of the first open prototypes, in operation since 1996, is the zeolite 13X storage system built in a school in Munich by ZAE Bayern [295]. The system was designed for peak shaving of the heating load in order to be operated jointly with district heating in winter to supply it during the off-peak in summer. The charging temperature is about  $130\,^{\circ}\text{C}$  while the storage capacity is  $1300\text{--}1400\,\text{kWh}$ . Heat released during the discharging mode is used to produce water vapor. A more recent prototype of ZAE Bayern was developed in 2015 [129]. It is an open system based on zeolite 13X for transportable sorption heat storage purposes. Waste heat from an incineration plant at  $130\,^{\circ}\text{C}$  is used as thermal source during discharging mode. The charging temperature was  $60\,^{\circ}\text{C}$  and a storage capacity of  $0.6\,\text{MJ/kg}$  was measured.

Among closed prototypes, one of the first was developed within the HYDES (High Energy Density Sorption Heat Storage) project [296]. The prototype in function from 1998 to 2001 was a solar thermal energy storage system for space heating purposes based on silica gel/H<sub>2</sub>O. Solar thermal collectors were used as low temperature heat source for the evaporator. The charging temperature was about 82 °C, the sorption one 32 °C, a power output of about 2.87 kW and 1.7 kW were measured during discharging and charging phase.

A prototype of closed system is currently being developed at GEPASUD laboratory (French Polynesia) [173]. It is a conventional mechanical vapor compression (MVC) driven by grid and PV electricity integrated with a thermochemical reactor based on the use of BaCl<sub>2</sub>/NH<sub>3</sub> as working fluids pair. The prototype has the aim to demonstrate that a thermochemical reactor coupled with a PV-driven mechanical compressor is an effective innovative solution offering energy storage capabilities for cooling purposes. The prototype uses ammonia not only as thermochemical material but also as refrigerant liquid. Among thermochemical storage materials, ammonia is expected to be established in the market for small and medium refrigeration [297–299].

The existing prototypes show a mature development of the TCTESs in heat-to-heat and heat-to-power applications. Collectors and concentrating solar plants (CSP) are mainly used as a heat source for the evaporator of the thermochemical devices. In particular, coupling storage into CSP systems enables dispatchable generation, whereby utilities produce power to match demand overcoming intermittency challenges faced by renewable energy production. Another field of wide application of TCTESs is the recovery of industrial waste heat [300–303]. Kuwata et al. [302] investigated the potential of the ammonium chloride SrCl<sub>2</sub> in applications based on utilization of industrial waste heat. Thermochemical energy storage could be a key technology able to bridge the gap between the wasted heat as the source and provided to customers at the time and place they need it [267,268]. A more detailed review on this field was developed in [304]. A list of some prototypes is given in Table 2 and in Table 3 for open and closed thermochemical systems respectively.

Appl. Sci. 2020, 10, 3142 11 of 35

**Table 2.** Example of prototypes of open systems for thermochemical storage.

		.ai storage.
Project Name/Institution	Description	Storage System
MONOSORP [305] (2006)	<ul> <li>Storage system for space heating</li> <li>Charging temperature T<sub>c</sub> = 20 °C</li> <li>Discharging temperature T<sub>d</sub> = 180 °C</li> </ul>	Zeolite 4A
Institute for Solar Technology SPF [241] (2006)	$\begin{array}{ll} \bigcirc & \text{Storage system for space heating.} \\ \bigcirc & T_c = 20  ^{\circ}\text{C} \\ \bigcirc & T_d = 180  ^{\circ}\text{C} \end{array}$	Zeolite 13X
ECN <sup>1</sup> [227] (2010)	<ul> <li>Lab scale packed bed reactor for seasonal storage of solar heat</li> <li>Discharge time about 25 h</li> <li>Storage energy density measured 0.14 MJ/kg</li> </ul>	MgCl <sub>2</sub> ·6H <sub>2</sub> O
CWS <sup>2</sup> [306] (2011)	<ul> <li>System integrated with a water tank (STES) for heating purposes</li> <li>T<sub>c</sub> = 35 °C</li> <li>T<sub>d</sub> = 180 °C</li> </ul>	LiCl with Zeolite 13X used as additive
ECN [211] (2013)	<ul> <li>Lab scale packed bed reactor for heating purposes (Heat Power 150 W)</li> <li>T<sub>c</sub> = 10 °C</li> <li>T<sub>d</sub> = 50 °C</li> </ul>	$MgCl_2 \cdot H_2O$
Energy hub-ECN [178,179] (2013–2014)	<ul> <li>Lab scale two packed bed modules for heating purposes</li> <li>T<sub>c</sub> = 70 °C</li> <li>T<sub>d</sub> = 185 °C</li> <li>Heat Power 400 W</li> </ul>	Zeolite 13X
ASIC <sup>3</sup> [176] (2014)	<ul> <li>Storage system for space heating and domestic hot water</li> <li>T<sub>c</sub> = 25 °C</li> <li>T<sub>d</sub> = 180 (230) °C</li> </ul>	Zeolite 4A (Zeolite 13X)
STAID <sup>4</sup> [180] (2015)	<ul> <li>Storage system integrated in a domestic ventilation system for space heating during peak hours</li> <li>T<sub>c</sub> = 57 °C</li> <li>T<sub>d</sub> = 120–180 °C</li> <li>Storage energy density 0.41 GJ/m³</li> </ul>	Zeolite 13X
ESSI <sup>5</sup> [276] (2016)	<ul> <li>Packed bed reactor for house heating</li> <li>T<sub>c</sub> = 25 °C</li> <li>T<sub>d</sub> = 80 °C</li> <li>Thermal power measured during sorption mode 0.3–0.8 kW</li> <li>Thermal power measured during desorption mode 0.4–1.6 kW</li> </ul>	SrBr <sub>2</sub> ⋅6H <sub>2</sub> O
STAID [181] (2016)	$\begin{array}{ll} \bigcirc & \text{Storage system for space heating} \\ \bigcirc & T_c = 20  ^{\circ}\text{C} \\ \bigcirc & T_d = 120180  ^{\circ}\text{C} \end{array}$	Zeolite 13X
NSFC <sup>6</sup> [159] (2017–2018)	<ul> <li>Lab-scale prototype experimentally investigated to store low-temperature heat for space heating</li> <li>T<sub>c</sub> = 20 °C</li> <li>T<sub>d</sub> = 30 °C</li> <li>Thermal power (56.7–136) W</li> </ul>	Activated alumina/LiCl

 $<sup>^{1}</sup>$  Energy Research Center of The Netherlands.  $^{2}$  Chemische WarmeSpeicherung.  $^{3}$  Austrian Solar Innovation Center.  $^{4}$  Stockage Inter Saisonnier de l'Energie Thermique dans les Batiments.  $^{5}$  European. Support to Social Innovation.  $^{6}$  Natural National Science Foundation of China.

**Table 3.** Example of prototypes of closed systems for thermochemical storage.

Project Name/Institution	Description	Storage System
SWEAT <sup>1</sup> /ECN [229] (2004)	<ul> <li>Solid sorption storage for cooling purposes.</li> <li>T<sub>c</sub> = 15-25 °C</li> <li>T<sub>d</sub> = 77-86 °C</li> <li>Thermal power measured in discharging mode 0.5-0.7 kW</li> <li>Thermal power measured in charging mode 1.2 kW.</li> </ul>	Na <sub>2</sub> S/H <sub>2</sub> O
MCES <sup>2</sup> [242] (2004)	<ul> <li>Solid sorption storage for cooling and heating purposes.</li> <li>T<sub>c</sub> = 65 °C</li> <li>T<sub>d</sub> = 80-95 °C</li> <li>Storage energy density 8 MJ/kg.</li> </ul>	Na <sub>2</sub> S·9H <sub>2</sub> O and graphite used as additive
MODESTORE [141,307] (2006)	<ul> <li>Storage system for heating purposes</li> <li>T<sub>c</sub> = 25 °C</li> <li>T<sub>d</sub> = 88 °C</li> <li>Thermal power measured during discharging mode 0.5 kW</li> <li>Thermal power measured during charging mode 1 kW.</li> </ul>	Silica gel
SOLAR-STORE [308] (2006)	<ul> <li>Solid sorption storage for heating and cooling purposes.</li> <li>T<sub>c</sub> = 35 °C</li> <li>T<sub>d</sub> = 80 °C</li> <li>Heating density power 47–49 kWh/m³</li> <li>Cooling density power 27–36 kWh/m³</li> </ul>	SrBr <sub>2</sub> with expanded natural graphite
SOLAR-STORE [278] (2008)	<ul> <li>Solid sorption storage for heating and cooling purposes.</li> <li>T<sub>c</sub> = 35 °C</li> <li>T<sub>d</sub> = 80 °C</li> <li>Heating power 60 kW</li> <li>Cooling power 40 kW</li> </ul>	SrBr <sub>2</sub>
Fraunhofher [136] (2012)	<ul> <li>Solid sorption storage for waste heat industrial recovery</li> <li>T<sub>c</sub> = 30 °C</li> <li>T<sub>d</sub> = 9-200 °C</li> <li>Heat storage capacity 0.54-0.79 MJ/kg</li> </ul>	Zeolite/CaCl <sub>2</sub>
E-hub/Project [190] (2012)	<ul> <li>Storage system for dwellings</li> <li>T<sub>c</sub> = 85–88 °C</li> <li>Heat density power 164 W/kg.</li> </ul>	Zeolite
E-hub/Project [189] (2014)	$\begin{array}{ll} \bigcirc & \text{Lab-scale prototype for space heating} \\ \bigcirc & T_c = 2030^\circ\text{C} \\ \bigcirc & T_d = 80120^\circ\text{C} \\ \bigcirc & \text{Storage energy density } 0.045\text{GJ/m}^3 \end{array}$	Zeolite 5A
COMTES <sup>3</sup> [309] (2015)	<ul> <li>Solid sorption system for space heating and domestic heat water.</li> <li>T<sub>d</sub> = 75 °C</li> <li>Storage energy density 0.4 GJ/m<sup>3</sup></li> </ul>	Zeolite 13XBF
COMTES [163] (2015)	$\begin{array}{ll} \bigcirc & \text{Liquid sorption system for diurnal storage} \\ \bigcirc & T_d > 50  ^{\circ}\text{C} \\ \bigcirc & \text{Power output approximately 1 kW} \end{array}$	NaOH/H <sub>2</sub> O

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Project Name/Institution	Description	Storage System
SJTU <sup>4</sup> [160] (2016)	<ul> <li>Solid sorption system for space heating and domestic heat water.</li> <li>T<sub>c</sub> = 40 °C</li> <li>T<sub>d</sub> = 85 °C</li> <li>Storage energy density 0.873 kWh/kg.</li> </ul>	LiCl with expanded graphite
HSR-SPF <sup>5</sup> [164] (2018)	$\begin{array}{ll} \bigcirc & \text{Liquid seasonal thermal storage system} \\ \bigcirc & T_c = 22  ^{\circ}\text{C} \\ \bigcirc & T_d = 50  ^{\circ}\text{C} \end{array}$	NaOH/H <sub>2</sub> O
Heat STRESS [170] (2019)	• Solid sorption system for seasonal thermal storage for domestic application $ T_c = 40~^{\circ}\text{C} $ • $T_d = 70~^{\circ}\text{C}$	CaCl <sub>2</sub> /NH <sub>3</sub>
University of Newcastle [245] (2019)  O Hybrid energy storage system to store end wind, solar and/or off-peak electricity sim Reaction take places a T > 800 °C		Co <sub>3</sub> O <sub>4</sub> /CoO
RESTRUCTURE [247] (2019)	<ul> <li>Pilot prototype integrated with Concentrated Solar Power (CSP) for power production</li> <li>Reaction take places in the temperature interval (800–1000) °C</li> </ul>	Co <sub>3</sub> O <sub>4</sub> /CoO

<sup>&</sup>lt;sup>1</sup> Salt Water Energy Accumulation and Transformation. <sup>2</sup> Modular Chemical Energy Storage. <sup>3</sup> Combined Development of Compact Thermal Energy Storage Technologies. <sup>4</sup> Institute of Refrigeration and Cryogenics (China) <sup>5</sup> Institute fur Solartechnik.

# 4. Thermochemical Storage in Power-to-Heat Applications

# 4.1. Thermochemical Storage Energy Systems in Power-to-Heat Applications: Case Studies

PtH technologies show a mature development with latent and sensible storage while only a limited number of applications with thermochemical storage is available in literature [310–317]. Existing applications focus on different aspects, hence a net comparison was not possible. Based on the usage of the heat stored, in this work the applications were divided into power-to-heat and power-to-heat-to-power as shown in Figure 4. In the first case, heat stored is used in the form of thermal energy for heating and cooling purposes. In the second case, heat, released during the discharging phase, is used to generate electricity when it is needed.

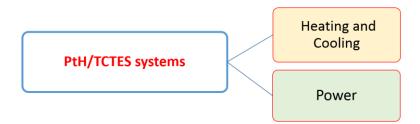


Figure 4. Thermochemical storage and power-to-heat uses.

Cammarata et al. [139] developed a hybrid thermochemical storage device to store the excess of power generation. The system was developed for household applications for low to medium temperature range (50–100  $^{\circ}$ C). The scheme of this case study is shown in Figure 5.

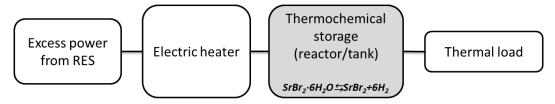


Figure 5. PtH/TCTES system developed by Cammarata et al. [139].

The system is based on the reversible hydration/dehydration of  $SrBr_2 \cdot 6H_2O$  and graphite as additive material. The power converted into heat by a heat pump driven by solar and wind energy is carried out to the tank storage where the endothermic dehydration reaction takes place at temperature < 100 °C. From the reaction  $SrBr_2$  (sorbent) and  $H_2O$  (sorbate) are formed ( $SrBr_2 \cdot 6H_2O \Rightarrow SrBr_2 + 6H_2O$ ), the sorbate is condensed for use in the discharging process in the case of closed system or released in the environment in the case of open system. Heat stored is use both heating demand and supply of electricity during the discharging phase. Their results showed that an energy storage density of 500 kJ/kg can be achieved at a temperature of 80 °C, a value of 600 kJ/kg by increasing the temperature to 150 °C. This study shows for the first time how the composite formulation of  $SbBr_2$  affects the energy density, heat and mass transfer and reaction kinetics.

Ferrucci et al. [173] developed a hybrid system for household applications. This integrates a thermochemical system with an air conditioning system driven by grid and photovoltaic electricity. The cooling system is a conventional Mechanical Vapor Compression (MVC) while the storage device is a packed-bed reactor with eight compartments based on the use of BaCl<sub>2</sub>/NH<sub>3</sub> as working pair. The scheme of this case study is shown in Figure 6.

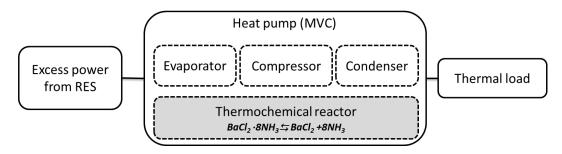


Figure 6. PtH/TCTES system developed by Ferrucci et al. [173] and by Fitò et al. [315].

When there is a surplus of electricity generation and no cooling needs, the extra power is used to run the compressor in order to store energy for later use. By means of a smart controller, during the storage process, the evaporator is disconnected from the circuit and the reactor is connected to the compressor. The desorption heat is provided by a low grade waste heat source at 50 °C or by an electric heater in direct contact with the thermochemical reactor. BaCl<sub>2</sub> reacts with ammonia (NH<sub>3</sub>) to form BaCl<sub>2</sub>·8NH<sub>3</sub> with an energy density estimated in an approximate value of 200 kJ per kg of reactor. The coefficient of performance, exergy efficiency and cooling capacity were used as indicators to compare a traditional MVC cycle without thermochemical storage and the hybrid system proposed. As example, the authors showed that the COP of the hybrid system, for a given source temperature, is higher than the one of a conventional one. The hybrid system was compared with alternative energy storage processes. In particular Pb and Li-ion batteries (electrochemical storage), ice and chilled water thermal storage was chosen as alternative devices to thermochemical reactor. Their results showed that the hybrid system proposed has a cooling capacity (60 Wh/L) six times larger than chilled water system but comparable to that one of ice storage systems. MVC systems with electrochemical batteries have the highest cooling capacity, 190 Wh/L for MVC and Pb battery and 420 Wh/L for MVC and Li battery respectively, but much shorter life span than MVC with thermochemical storage. The COP of the hybrid system (4.8) is comparable to Pb batteries (4.2), Li-ion batteries (4.2) and chiller (4.2) systems.

The hybrid system is an example of compressor-driven method for energy storage and deferred cooling. This application for space cooling is not yet widely explored in literature.

Fitò et al. [315] analyzed an ammonia-based refrigeration system consisting in the hybridization of compression refrigeration with thermochemical storage. The proposed hybrid system has the typical architecture of a MVC cycle (evaporator, compressor, condenser, reservoir and throttling valve), a grid-connected photovoltaic installation and a thermochemical storage reactor. The scheme of this case study is shown in Figure 6.

MVC cycle and thermochemical storage system have the same condenser, evaporator and refrigerant fluid (NH<sub>3</sub>). The storage device is a packed-bed reactor based on the use of  $BaCl_2/NH_3$  as working pair. Both the PV installation and the grid are used to meet the electricity requirements for cold production. When there is a surplus of power generation from RES and no cooling demand, the power in excess is used to store energy in the form of heat driving the desorption phase of the reactor. Thermochemical process enables the storage of energy in the form of chemical potential for a deferred cold production without running the compressor. The heat of desorption is provided by waste heat or solar collectors at about 50 °C. The authors demonstrated an overall thermochemical cycle has a COP (1–1.4) higher than a conventional MVC operating without thermochemical storage.

Finck et al. [175] developed a hybrid compression thermochemical refrigeration system (HCTSR) to show the potential power flexibility of thermal storage and power-to-heat.

Power flexibility is in this specific case defined as the thermal response of TES tanks and related electricity consumption of the heat pump during charging, discharging and store mode. The scheme of this case study is shown in Figure 7.

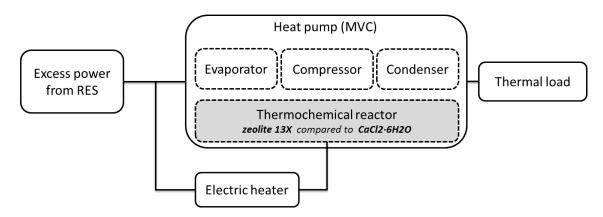


Figure 7. PtH/TCTES system developed by Finck et al. [175].

HCTRS, consists of an MVC cycle and a thermochemical reactor. The heat pump and an electric heater serve as power-to-heat conversion while the storage tank as the source of flexibility. The thermochemical storage device is a packed bed reactor based on zeolite 13X and water as working pair. During desorption, the electric heater serves as a dehydration source. During adsorption, the heat stored is used for space heating or domestic hot water. The system with thermochemical storage was compared with the one obtained coupling the same MVC to a sensible and latent storage tank. Water and  $CaCl_2 \cdot 6H_2O$  were used as sensible and latent material respectively. Results show that assuming the same dimensions for the storage tank (a cylindrical vessel of 0.5 m³) and a volume flow of heat transfer medium of 1 m³/h, the thermochemical system has an energy capacity (0.05 GJ) lower than the other storage systems (0.15 GJ). The available storage capacity (COC) and storage efficiency ( $\eta_{OC}$ ) were used to compare the energy flexibility of the three different thermal storage systems. COC is defined as the amount of energy that is shifted during the optimal control to minimize the electricity consumption costs for operating the heat pump and the electric heater.  $\eta_{OC}$  indicates the effective use of the heat stored to compensate power-to-heat devices during optimal control. Results show that the thermochemical storage has the lower values for both COC (5.6 kWh) and  $\eta_{OC}$  (0.96).

Appl. Sci. 2020, 10, 3142 16 of 35

The following studies are examples of power-to-heat-to-power applications in which the heat stored is converted into electricity by a power plant when it is needed.

Wu et al. [245] proposed a hybrid energy system to store excess energy from renewable sources. The system consists of a compressed air energy storage (CAES) integrated with a thermochemical reactor based on the use of the metal oxide redox pair  $\text{Co}_3\text{O}_4/\text{CoO}$  as sorption working material. In contrast to a conventional Compressed Air Energy Storage (CAES) [317] in which compressed air is superheated by means the combustion of fossil fuel, in the proposed hybrid system this function is replaced by the sorption reactor. The scheme of this case study is shown in Figure 8.

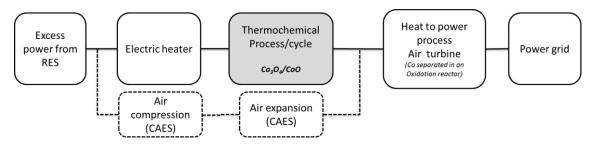


Figure 8. PtH/TCTES system developed by Wu et al. [245].

The proposed system consists of five compressors powered by electricity to compress air and an electric heater as heat source for the charging phase of the thermochemical storage process. The thermal charging phase takes place, in parallel with the CAES compression phase, with the reduction of  $Co_3O_4$  into CO and  $CO_2$  ( $2Co_3O_4 \leftrightarrows 6CoO + O_2$ ) carried out at 870 °C and 0.1 bar. The discharging phase takes place and the energy stored in the compressed air and metal oxide CoO (heat released by the exothermic reaction is transferred to air) is converted back into electricity throw air turbines. A value of 3.9 kWh/m³ was evaluated for the energy storage density, defined in this case as the total power output per unit volume of the stored air (the same as the volume of the storage cavern). Moreover, it was estimated that 65% of the energy storage density relies on thermochemical part of the system while the remaining 35% is achieved via the CAES. The authors demonstrated that, in terms of storage energy density, the hybrid system has a value comparable to a conventional CAES (3–6 kWh/m³) operating at the same conditions. Based on a thermodynamic analysis it was estimated an efficiency of 56.4%. In comparison to conventional CAES plants, authors showed that this value is higher than the efficiency of the commercialized Huntfort (42%) and McIntosh (54%) CAES plants.

Fernandez et al. [235] developed a power-to-heat-to-power system based on the calcination/carbonation of calcium carbonate as sorption process and a closed  $CO_2$  Brayton regenerative cycle. The scheme of this case study is shown in Figure 9.

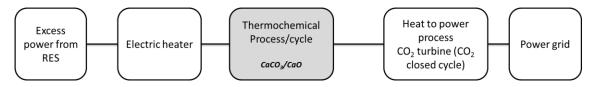


Figure 9. PtH/TCTES system developed by Fernandez et al. [235].

During the charging phase, the electric power is converted into thermal power by Joule effect to heat up the calciner (Fluidized bed thermochemical reactor). In the reactor the calcination endothermic reaction takes place under atmospheric pressure at 950 °C, CaO and CO<sub>2</sub> are formed (CaCO<sub>3</sub>  $\leftrightarrows$  CaO + CO<sub>2</sub>). During the discharging phase, that takes place at 75 bar and 25 °C, power is generated in a CO<sub>2</sub> turbine connected to an asynchronous generator that converts mechanical power into electricity. CaO and CO<sub>2</sub> are carried out in the carbonator reactor where the exothermic carbonation reaction occurs. The presence of a calciner and a carbonator is indicative that in the system charging and discharging

Appl. Sci. 2020, 10, 3142 17 of 35

cycles are well differentiated and independent. The system is connected to the grid to export electrical power generated during the discharging phase. The proposed system was simulated under different charging and discharging operations modes to assess its potential as large-scale electric energy storage system estimating a maximum reachable efficiency of 39%.

Wu et al. [316] developed a phase change redox (PCR) system to convert electricity surplus into heat and to store it using a CuO/Cu<sub>2</sub>O cycle. The scheme of this case study is shown in Figure 10.

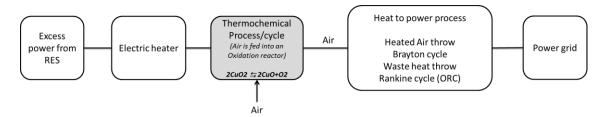


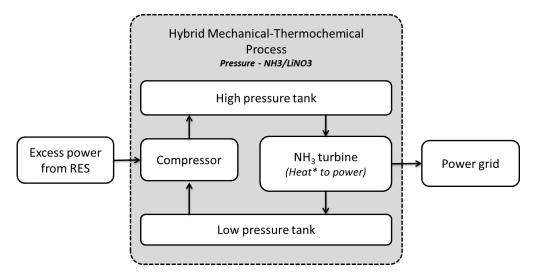
Figure 10. PtH/TCTES system developed by Wu et al. [316].

When there is a surplus of electricity from grid or solar/wind plants heat provided by Joule heating is used for the charging phase of the sorption process. During this phase,  $CuO_2$  is reduced into CuO and  $O_2$  ( $2CuO_2 \leftrightarrows 2CuO + O_2$ ). The molten  $CuO/CuO_2$  requires a high temperature of about 1200 °C during the charging phase. When electricity demand in the grid occurs the discharging phase starts. During this phase, the exothermic reaction takes place and the stored molten  $CuO/CuO_2$  is oxidized and cooled into an oxidation reactor using air. Heated air is used into a Brayton cycle coupled with a bottoming organic Rankine cycle (ORC). Energy storage density and round trip efficiency were the indicators used to assess the energy storage performances. Energy storage density is here defined as the heat stored per mass unit of the raw material CuO while the round trip efficiency is the amount of electricity that can be recovered for a given energy input. The PCR system coupled to the Brayton and Rankine power generation cycles is able to achieve a round trip efficiency of about 50%. Advantages of the proposed PCR system are high-energy storage density, high round trip efficiency, enhancement of  $CuO/Cu_2O$  reversibility, abundant and low-cost raw material and oxygen as a valuable by-product. The main disadvantages and potential limits can be summarized as systems complexity, high-temperature heat source, high operating temperature and high equipment, operation and maintenance costs.

Rodriguez et al. [318] proposed an innovative hybrid absorption system based on the thermochemical technology to store electrical energy at large scale. The system consists of two storage tanks to accumulate a liquid solution at two different levels of pressure, a compressor powered by the excess renewable energy, a thermochemical storage tank (using of NH<sub>3</sub>/LiNO<sub>3</sub>, where NH<sub>3</sub> is the solute while LiNO<sub>3</sub> is the sorbent) and an independent vapor expander/turbine (T) located between the high and low pressure tanks that drives an electrical generator. The scheme of this case study is shown in Figure 11.

When there is an excess of renewable electricity generation, the charging phase takes place increasing the pressure difference between the two reservoirs. The authors highlighted that the amount of energy required to pressurize the gas in the proposed hybrid cycle is lower than pressurizing a gas with no phase change. During the discharging phase, the turbine transforms the stored energy into mechanical energy driving a generator and returning the electricity into the grid. Numerical simulations were carried out in order to evaluate the performance of the storage system. For a nominal renewable power of 18 kW and an energy output of 8 kW, 44.3% and 0.36 MWh were the values found for the efficiency and energy storage respectively. The viability of using of an absorption thermochemical energy stored system inherently combined with a gas compression cycle was demonstrated only theoretically.

The features of the cases described in this section are summarized in Table 4.



**Figure 11.** PtH/TCTES system developed by Rodriguez et al. [318]. \* Heat is exchanged between the two tanks in order to compensate the ammonia expansion/compression cycle.

References	Application	Storage Material	Performance Indicators
Cammarata et al. [139]	Power-to-heat (household application)	SrBr <sub>2</sub> /H <sub>2</sub> O	Energy density: 500 kJ/kg
Ferrucci et al. [173]	Power-to-heat (integrated into electric driven cooling system)	BaCl <sub>2</sub> /NH <sub>3</sub>	Energy density: $200 \text{ kJ/kg}$ COP = 4.8
Finck et al. [175]	Power-to-heat (integrated into electric driven cooling system)	Zeolite 13X/H <sub>2</sub> O	Capacity: 5.6 kWh Efficiency: 0.96
Wu et al. [245]	Power-to-heat (to power)	Co <sub>3</sub> O <sub>4</sub> /CoO	Energy density: 3.9 kWh/m <sup>3</sup> Efficiency: 56.4%
Fernandez et al. [235]	Power-to-heat (to power)	CaCO <sub>3</sub> /CaO	Overall plant Efficiency: 39%
Wu et al. [316]	Power-to-heat (to power)	CuO/Cu <sub>2</sub> O	Energy density: 1600 kJ/kg Efficiency: 50%
Rodriguez et al. [318]	Power-to-heat (to power)	NH <sub>3</sub> /LiNO <sub>3</sub>	Capacity: 0.36 MWh Efficiency: 44.3%

**Table 4.** Thermochemical storage in PtH and PtH/HtP applications.

#### 4.2. Discussion and Outlook

The articles reviewed show emerging power-to-heat/thermochemical applications as flexible coupling systems to address both integration of renewable energies and additional grid flexibility. High efficiency in balancing the excess of renewable generation is the key aspect that could led these applications towards an increasing development in the next future.

Investigating the demand flexibility of power-to-heat conversion with thermochemical systems was a common aim of all authors. All three dimensions of flexibility were investigated: size (energy), time (power) and costs. A number of indicators were proposed to quantify the energy flexibility in terms of available storage capacity and/or efficiency. The usage of a non-common quantification method to estimate the energy flexibility makes difficult a straightforward comparison among the reviewed studies. Despite this limit, important considerations can be argued as follows.

According to the thermodynamic and numerical analyses, the overall efficiency of the coupled system range from 39% to 56%. The highest value is obtained in power-to-heat/thermochemical applications coupled to power cycle [317], overcoming typical efficiencies of conventional power cycles. The reason lies in the use of raw thermochemical materials requiring higher operating temperatures, which increase the upper limit of the achievable thermodynamic efficiency according to Carnot

principles. This suggests that more efforts should be paid to the design and test of thermochemical materials and related physical–chemical reactions, in order to boost further the process efficiency in view of the development of optimized systems.

The studies reported in [246,317] suggest that the high efficiency and flexibility of these innovative applications could be able to facilitate the integration in the power system not only of the photovoltaic but also of the wind power. A development in the wind energy integration could be crucial in energy systems characterized by a large share of wind power.

High storage density, low heat loss, long storage period, highly compact energy storage are the main advantages common to all the power-to-heat/thermochemical technologies. Despite this, a series of limits, such as the high costs of the materials and the complexity of the equipment, makes these applications still not mature for large scale/market adoption as shown by the few prototypes developed and tested so far. Costs abatement and process simplification in optimized systems require further efforts for the development of techno-economically competitive applications. Moreover, the deployment at large-scale of these potential low-carbon technologies will require significant investments and the revision of the present infrastructures.

#### 5. Conclusions

In this work, to provide a comprehensive review on the state of art of thermochemical storage systems and their applications in power-to-heat technologies, theoretical, experimental and numerical studies and their recent advancements and potential perspectives were discussed.

This paper reviews the current literature that refers to the development and exploitation of thermochemical storage systems connected to power-to-heat technologies to power grid support. The operation principles both of thermochemical and of power-to-heat are presented, thermochemical materials and processes are compared. Power-to-heat conversion is likely the most mature and favorable technology enabling power flexibility. It is particularly suitable in energy systems with high shares of renewable generation. In order to increase the flexibility of the energy system, power-to-heat technologies coupled to thermal storage devices are among the most promising alternatives. Thermal storage is able to provide several benefits such as load management, power quality and continuous power supply. When there is an excess of generation, electricity is converted into heat and stored for subsequent use on demand. In this way, additional power in the situations of increased load is provided, thus contributing to peak shaving, load shifting and energy conservation. The conversion of power into heat is generally performed by electrical resistances or via heat pumps. Despite converting electric power into heat is not convenient from a thermodynamic perspective, power-to-heat applications are gaining an increasing attention due to the low prices of renewable electricity and the increasing surplus of produced electricity that cannot be used. Several advantages, e.g., high efficiency for balancing excess renewable generation and high potential on reduction of CO<sub>2</sub> emissions and fossil fuels, could be the key elements for a larger development in the future trends of these technologies.

There are several examples of sensible and latent thermal storage in power-to-heat applications, while only a limited number of applications of thermochemical storage in the power-to-heat field are available. High energy storage density, no heat loss during the storage, no self-discharge and long charge/discharge, broad availability and suitable temperature ranges are some important advantages of thermochemical storage systems.

However, the high complexity and costs of these technologies limit the real applications, while only few prototype-scale systems have been studied. To improve their implementation, comprehensive analyses and investigations are further required. In contrast, thermochemical storage is widely used into heat-to-power sector. Heat-to-power and power-to-heat sectors are among the most relevant options available to balance fluctuating renewable energy sources and hence power grid. This particular interaction between electricity and heat sectors will play an important role towards the cost effective transition to a low carbon energy system with a high penetration of renewable generation.

Appl. Sci. 2020, 10, 3142 20 of 35

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#### Nomenclature

AB Storage material
A,B Reaction products
ALPOs Aluminophosphates

CAES Compressed air energy storage

Cp Heat capacity (J/(kg K))
CHP Combined heat and power
COP Coefficient of Performance

CSP Collectors and Concentrating Solar Plant

DHS District heating systems
DSM Demand-side management  $\Delta h \qquad \text{Phase change enthalpy (°C)}$   $\Delta H \qquad \text{Standard reaction enthalpy (J/mol)}$   $\Delta S \qquad \text{Standard reaction entropy (J/(°C mol))}$ 

ΔT Temperature difference (°C)

GHG Greenhouse gases

HCTSR Hybrid compression thermochemical refrigeration system

HPs Heat pumps HtP Heat to power

LTES Latent thermal energy storage

m Mass (kg)

MVC Mechanical vapor compression

ORC Organic Rankine cycle
PCM Phase change materials
PCR Phase change redox
PtH Power-to-heat
PV Photovoltaic

 $\begin{array}{lll} \text{PV-CaL} & \text{Photovoltaic Calcium looping} \\ \text{Q}_l & \text{Latent energy stored (J)} \\ \text{Q}_s & \text{Sensible energy stored (J)} \\ \text{RES} & \text{Renewable energy sources} \\ \text{SAPOs} & \text{Silico-aluminophosphates} \\ \text{STES} & \text{Sensible heat storage} \end{array}$ 

T Turbine

 $\begin{array}{ll} T_c & \quad & \text{Charging temperature (°C)} \\ T_d & \quad & \text{Discharging temperature (°C)} \end{array}$ 

TCTES Thermochemical thermal energy storage

TES Thermal energy storage

TESs Thermal energy storage systems VRE Variable renewable electricity

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Appl. Sci. 2020, 10, 3142 30 of 35

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Appl. Sci. 2020, 10, 3142 31 of 35

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Appl. Sci. 2020, 10, 3142 34 of 35

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Appl. Sci. 2020, 10, 3142 35 of 35

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