

**Manuscript version: Author's Accepted Manuscript**

The version presented in WRAP is the author's accepted manuscript and may differ from the published version or Version of Record.

**Persistent WRAP URL:**

<http://wrap.warwick.ac.uk/156576>

**How to cite:**

Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

**Copyright and reuse:**

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

© 2021 Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International <http://creativecommons.org/licenses/by-nc-nd/4.0/>.



**Publisher's statement:**

Please refer to the repository item page, publisher's statement section, for further information.

For more information, please contact the WRAP Team at: [wrap@warwick.ac.uk](mailto:wrap@warwick.ac.uk).

**Lithium compounds for thermochemical energy storage: A state-of-the-art review  
and future trends**

Paula E. Marín<sup>1,2</sup>, Yanio Milián<sup>2</sup>, Svetlana Ushak<sup>2\*</sup>, Luisa F. Cabeza<sup>3</sup>, Mario Grágeda<sup>2</sup>,  
Stan Shire<sup>1</sup>.

<sup>1</sup>*School of Engineering, University of Warwick, Coventry CV4 7AL, United Kingdom*

<sup>2</sup>*Department of Chemical Engineering and Mineral Processing, and Center for Advanced  
Study of Lithium and Industrial Minerals (CELiMIN), Universidad de Antofagasta, Campus  
Coloso, Av. Universidad de Antofagasta, 02800 Antofagasta, Chile*

<sup>3</sup>*GREiA Research Group, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain*

*\*Corresponding author: svetlana.ushak@uantof.cl*

**Abstract**

**Keywords:** *lithium compounds; thermochemical storage; patents; technological and cost  
challenges; energy storage density; TCS operational conditions.*

24	<b>Contents</b>
25	<b>1. Introduction</b>
26	<b>2. Lithium sources, abundance, and production</b>
27	<b>3. Thermochemical energy storage (TCS) systems</b>
28	<b>4. Lithium compounds for TCS. Advances in the scientific research</b>
29	<b>4.1 Lithium in TCS. Chemical reactions</b>
30	<b>4.2 Lithium in TCS. Sorption</b>
31	<b>5. Lithium compounds for TCS. A new look from patents</b>
32	<b>6. Future trends. Proposed Li materials for TCS</b>
33	<b>6.1 Technological and economic challenges</b>
34	<b>6.2 Environmental challenges</b>
35	<b>7. Conclusions</b>
36	<b>8. References</b>
37	
38	
39	
40	
41	
42	
43	
44	
45	
46	
47	

## 1. Introduction

In the last 20 years, the world has undergone significant changes in technology, generating vital products for the functioning and development of society [1]. Due to our dependence on technology and the sources of energy required by these products, the development of strategies to store and supply energy are nowadays considered equally crucial for the expansion of such technologies. Additionally, the impacts of greenhouse gas (GHG) emissions and climate change are exerting pressure towards less polluting sources of energy and strategies to diminish energy losses [2].

Lithium has become a milestone element as the first choice for energy storage for a wide variety of technological devices (e.g. phones, laptops, electric cars, photographic and video cameras amongst others) [3] and batteries coupled to power plants [4]. As a consequence, the demand for this mineral has intensified in recent years, leading to an increase in the industrial production. As a result, during the period 2009 - 2019, the world mining production of lithium increased from 18,000 to 77,000 metric tons respectively; this represents more than 4 times as much production in 2019 compared to that reported in 2009, the largest producers of this mineral being Australia and Chile with 42,000 and 18,000 metric tonnes in 2019, respectively [5,6].

Even though batteries for energy storage are one of the main applications of lithium compounds, either in technological devices or as a reserve for energy supply in power plants, this is not the exclusive way of applying lithium compounds. Lithium compounds are also an attractive alternative to store energy in thermal energy storage (TES) systems.

TES materials, including lithium compounds [7], play a strategic role in TES systems for industrial waste heat recovery [8–10], concentrated solar power (CSP) plants [11–13], and buildings [14–16] amongst other applications, due to their large heat storage capacity [17]. There are three technologies for TES systems: (i) sensible heat storage (SHS) that is based on storing thermal energy by raising the temperature of a liquid or solid storage medium (e.g. water, sand, molten salts, rocks), with water being the most common option; (ii) latent heat storage (LHS) using phase change materials or PCMs to store heat via a change of state (e.g. from a solid state into a liquid state); and (iii) thermo-chemical storage (TCS) using chemical reactions to store and release thermal energy [18]. Within the three types of TES, the main advantages of using TCS systems are the high-energy density of storage they provide, as well as the possibility of storing energy in the long-term without significant losses [19], as the reactants (energy storing materials) can be stored at ambient temperature.

Due to the high-energy density of TCS systems, it is expected the application of such technologies in solar plants, in residential and commercial buildings, as well as their use for heating or cooling buildings [20]. Some examples of working pairs (the two reactants that store heat as chemical energy) applied in TCS are the hydration reactions of salts such as NaOH and water [21], SrBr<sub>2</sub> and water [22], the cyclical behaviour of MgSO<sub>4</sub> and its dehydration [23], the storage of thermal energy based on Ca(OH)<sub>2</sub> and the cycle of CaO [24]. The potential of such chemical reactions places thermochemical energy storage as one of the most advantageous techniques for storage in CSP plants [25]. In the last 3 years, there has been an increasing number of reviews related to thermochemical energy storage in scientific journals. These reviews not only focus on applications of the TCS systems, but also on the

materials assessed, which are referred to as thermochemical materials. An example of this is the review by Koohi-Fayegh and Rosen [26] which conducted an evaluation on types of energy storage, including TCS systems and applications. However, there are more specific reviews made according to the type of application, such as concentrated solar power plants (CSP) [25,27–30], high-temperature TCS systems [31–33], power grid support [34], building applications [35] and evaluation of thermochemical material for their implementation in TCS systems [36–40].

Although TCS has been studied and developed, there are still problems associated with performance and implementation. The issues associated with TCS can be partially solved by investigating materials for new working pairs applied in such systems. In this sense, lithium is considered a novel and promising alternative as thermochemical material, with potential to improve the specific heat capacity of a system [7]. This has been demonstrated by Kiplagat et al. [41] and Ishitobi et al. [42]. Kiplagat proposed a consolidated composite material made from expanded graphite (EG) powder impregnated with LiCl salt for use in solar-powered adsorption ice makers. Similarly, Ishitobi studied the dehydration and hydration reactions corresponding to the heat storage and the heat output operations of authentic  $\text{Mg}(\text{OH})_2$  and LiCl-modified  $\text{Mg}(\text{OH})_2$  as a potential new material for chemical heat pumps – device that allows the transfer of heat energy. Despite the positive results of lithium compounds as TCS, information about the current research position and future outlook for such technologies is still lacking.

Considering the above mentioned, there is a clear need to have more and more systematic information about the potential of lithium as a thermochemical material and the implications

for this element as an alternative material in TCS technologies. Hence, the objective of this review is to investigate the current state of development of lithium applications in TCS systems. This work is based on relevant criteria, discussing and analysing factors related to the abundance of the resource, establishing key properties to determine the most suitable materials depending on the application, assessing the economic context and forecasting future trends of such technologies in terms of their potential applications and environmental challenges. Additionally, to complement the information obtained from scientific articles, a search was made for available patents related to the latest technological developments based on lithium compounds applied in TCS systems.

## **2. Lithium sources, abundance, and production**

One relevant criterion to assess the applicability of specific materials is the abundance and availability of the resource. The abundance of a material will broadly impact the potential for exploitation and the capacity to maintain a relatively secure stock. The availability refers to the accessibility of a resource. In this respect, lithium abundance and production levels are continually monitored by several governmental agencies, and treated as a key commodity [6].

Lithium is the lightest metal with the lowest density of solid elements on the periodic table. It has a high electrical and thermal conductivity, low viscosity, and shows a low coefficient of thermal expansion. Due to lithium's reactivity, this element is not found naturally in its pure metallic form but mainly in minerals and brines, from which it is extracted to be converted into a variety of lithium-containing compounds and derivatives [43]. According to

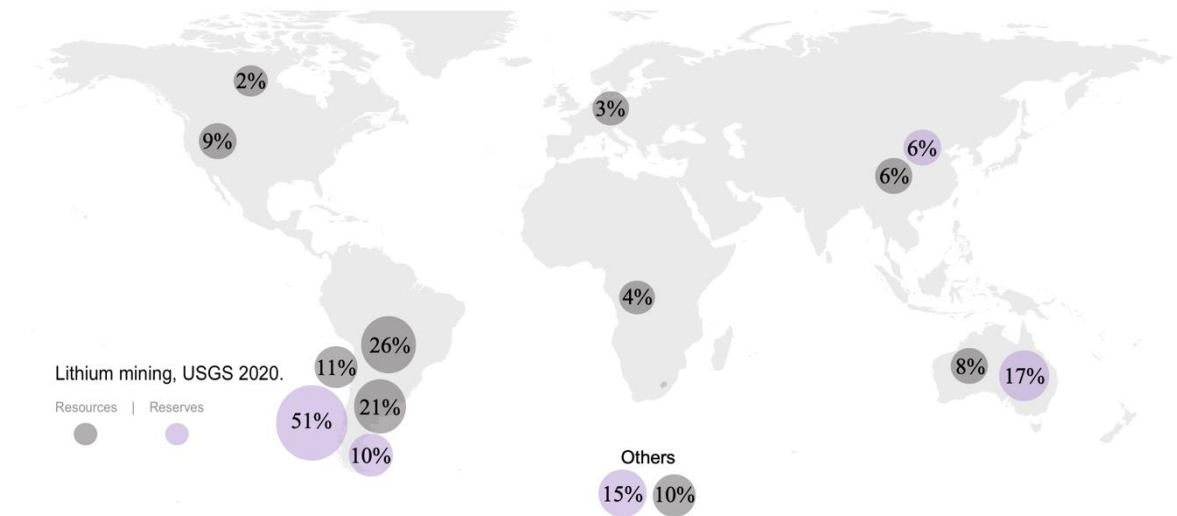
the United States Geological Survey (USGS), the main sources of lithium are in closed-basin brines (58%), pegmatite rocks and granites (26%), lithium-clays (7%), oilfield brines (3%), geothermal brines (3%), and lithium-zeolites (3%) [44].

In the 2018 USGS report and the latest update released during 2019, known lithium resources – a non-defined amount of discovered and undiscovered geological deposit – and reserves – subgroup of resources already discovered, having a known size and being a profitable geological deposit – have grown by 22.8% and 16.1% respectively [45]. In 2019, lithium reserves reached 16.6 million tons – total reserves –, compared to 13.9 million tons of mineral in the previous period, a growth that was mainly caused by the increase in reserves cyphers of Chile, USA, and Canada. In terms of resources, the USGS reported the largest resources in Bolivia, Argentina, and Chile, with Bolivia being the country that reported the greatest progress, going from 9 to 21 million tons – one ton of lithium equates to 5,323 tons of lithium carbonate. In the same year, the global lithium mine production was 77,000 ton, representing around 0.5% of the total reserves [6].

The world's largest reserve of lithium is located in Chile, with 51% of the total, followed by Australia, with 17%, and Argentina, with 10%. In terms of resources, Bolivia (26%) and Argentina (21%) account for 47% of the total, while Chile represents 11% (Figure 1) [6]. The three aforementioned South American countries form the so-called “lithium triangle”, where the brines of Argentina, Bolivia, and Chile are located, which together represent more than 80% of the resources in brines and more than 50% of the total resources [46]. Although there are countries with abundant resources, it is not necessarily economically feasible to



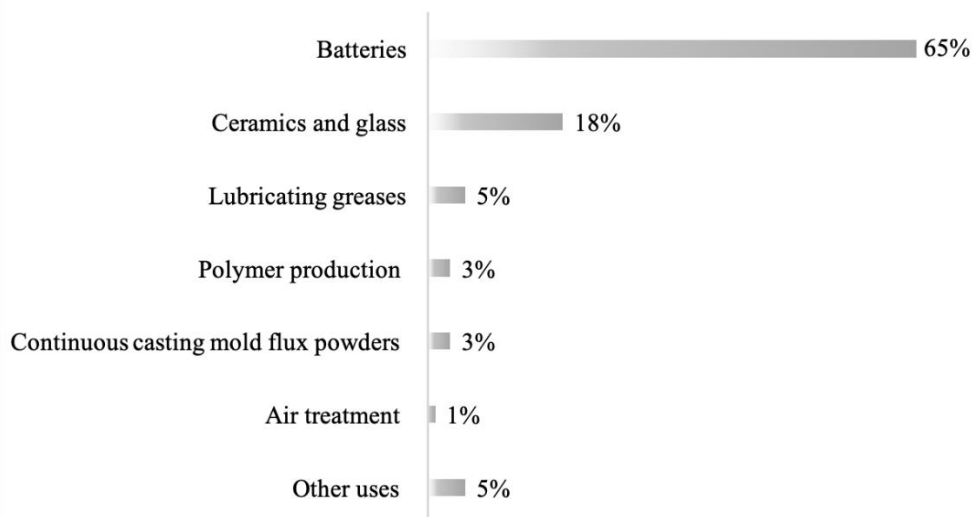
exploit them because poor accessibility and levels of impurities such as magnesium and iron [44].



**Figure 1.** Geographical distribution of the main reserves and resources of lithium, 2019. (Countries within reserves: Chile, Australia, Argentina, and China, others: USA, Canada, Zimbabwe, Brazil, and Portugal; Countries within resources: Bolivia, Argentina, Chile, USA, Australia, China, Congo, Germany, and Canada, others: Mexico, Czech Republic, Mali, Russia, Serbia, Zimbabwe, Brazil, Spain, Portugal, Peru, Austria, Finland, Kazakhstan, and Namibia) [6].

Lithium has various uses, the most widespread being in lithium-ion batteries, with applications in cell phones, laptops, power tools, and hybrid or electric vehicles, amongst others. Moreover, there are other applications for lithium that are not as well-known but equally important (Figure 2), such as in glass and ceramic aggregates to make them more resistant to changes in temperature. Lithium is also used in fats and oils that resist heat, in alloys with aluminium and copper to lighten structural components for the aeronautical

industry, in the manufacture of polymers, in air filters and many other applications, in which the medicinal ones stand out, such as psychotropic drugs usually perceived as a mood stabilizer [6].



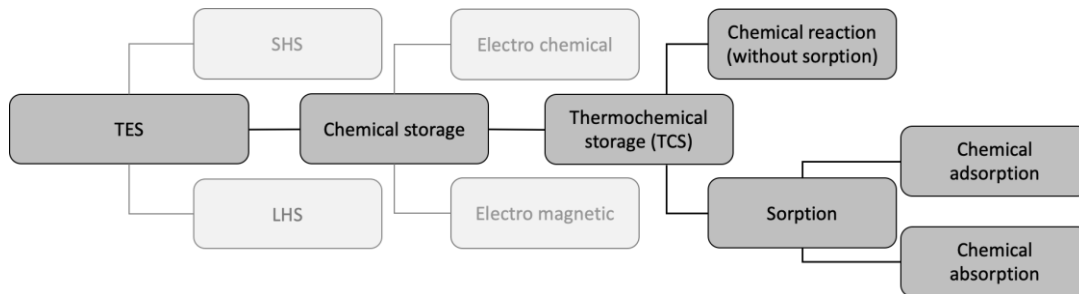
**Figure 2.** Lithium end applications, 2019 [6].

The use of lithium in rechargeable batteries for the automotive industry constitutes a potential benefit for the world population and the environment since they would make it possible for vehicles to use energy from renewable carbon-free sources (e.g. solar, hydroelectric or wind power) instead of traditional fuel sources (e.g. naphtha, diesel) reducing carbon dioxide emissions, a pollutant considered to be one of the main causes of global warming [47].

### 3. Thermochemical energy storage (TCS) systems

TCS systems are a form of chemical storage, and a part of a much wider group of TES technologies, which also includes SHS and LHS (Figure 3). In the literature it is possible to find multiple schemes of classification of TCS systems [48,49]. As shown in Figure 3, TCS

systems are typically divided into *chemical reactions* and *sorption*. Nonetheless, sorption systems do not exclude the involvement of chemical reactions as a basis for the operational mechanisms of such approach. Thus, sorption applications are further divided into chemical adsorption and chemical absorption; adsorption refers to the molecular assimilation within the bulk of a solid or liquid, and absorption to the accumulation of molecules on the surface of a solid or liquid. The present classification was proposed by Yu et al. [50], work that illustrates the many problems in relation to the conceptual ambiguities, classification issues and the abundance of terms and expression without proper description or statement to facilitate a common understanding.



**Figure 3.** Scheme of TES classification based on Yu et al. [50].

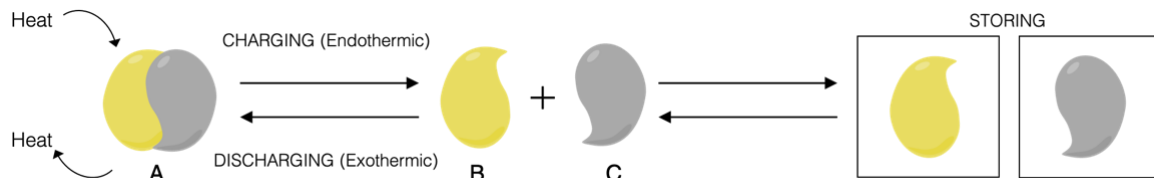
The functionality of TCS systems is based on the performance of a reversible chemical reaction (or desorption), that allows the storage of heat during the decomposition process, which has an endothermic nature, whereas the reverse synthesis reaction is exothermic and results in returning the stored heat [51]. All reversible physicochemical reactions within TCS systems can be explain by Eq. 1, in which A is a reactant thermochemical material (TCM) that in the presence of a heat supply can be decoupled into products, components B and C. These products can be of any phase and stored separately and are reactive as working pairs

or sorption pairs. The reaction between the products B and C will restore the reactant A and release heat as result of this reaction [52].



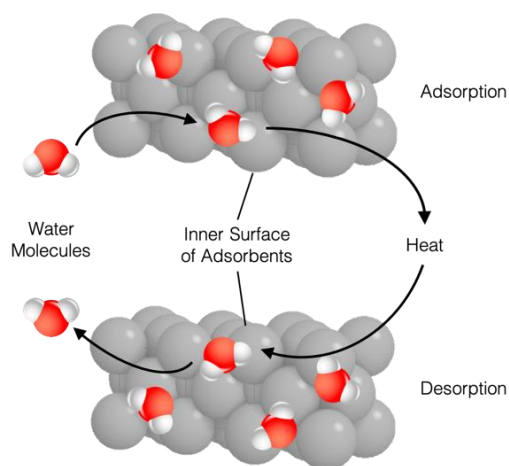
This classical TCS system is divided into three main processes, as shown in Figure 4:

- (i) **Charging:** The charging process is carried out through an endothermic reaction, where thermal energy is absorbed and is used to dissociate thermochemical material A, into two materials that can be stored, B and C.
- (ii) **Storage:** After the charging process, the materials obtained B and C, are stored separately until energy is required. Materials are generally stored at room temperature, and the small loss that may occur is due to the degradation of the materials.
- (iii) **Discharge:** In this stage, an exothermic reaction occurs from combining materials B and C, the energy that had been stored is released as heat and the original thermochemical material A, is formed again.



**Figure 4.** Diagram of the processes involved in the TCS cycle.

As previously explained, TCS can be classified into chemical reactions and sorption processes (Figure 3) [50]. TCS based on chemical reactions is characterised by a change in the chemical bonds of the compound involved in the reaction (dissociation and recombination), the energy can be stored through the endothermic reaction and released by the reverse exothermic reaction. Whilst, sorption storage is defined as a phenomenon of binding of a gas or vapour by a sorbent substance in a condensed state (solid or liquid) through less intense interactions. Sorption processes can involve thermophysical and thermochemical aspects [53]. The adsorption and desorption process on solid materials is schematically shown in Figure 5. In the adsorption step, binding of a gaseous or liquid phase of a component occurs on the inner surface of a porous material. Then, during the desorption stage –energy charging step– heat is put into the sample, driving out the adsorbed component (e.g. water molecules in Figure 5) from the inner surface. In the reverse reaction (i.e. adsorption), the sorbate, in this case water molecules are adsorbed, and the heat stored in the system during desorption will be released. The adsorption step represents the discharge process.



**Figure 5.** Adsorption and desorption process of water vapour on solids [54].

The main advantages of thermochemical storage systems are their high storage density (0.5-3 GJ/m<sup>3</sup>) and negligible heat losses over long periods [19]. Evidence of this potential is the existence of hybrid cars that run on electrical energy and thermochemical energy, a project that is currently on the pilot phase of development [55]. However, TCS systems are not flawless, and the main drawbacks of such thermochemical storage technologies account for; high cost, inappropriate operating temperatures, ineffective power discharge for certain applications due to low kinetic reactions and low discharge temperature near-equilibrium point, and parasitic losses to sensible heating resulting in low/moderate efficiency of storage cycles [56]. This is why a series of parameters must be carefully considered before selecting a thermochemical material so that its use is appropriate for the type of storage required.

#### **4. Lithium compounds for TCS. Advances in the scientific research**

In order to incorporate most of the current available literature related to lithium application in TCS, multiple searches were carried out on databases from *SCOPUS* and *Web of Sciences*. In the search, the following Boolean were utilised: *Web of Science* - lithium\* AND Thermochemical Storage\*; *Scopus*; - “lithium” AND “Thermochemical Storage”. The criteria of selection are presented in Figure 6. The search included articles available until August 2020.



**Figure 6.** Flow diagram presenting retrieved studies from search in *Scopus* and *Web of Sciences*. Literature search include several criteria for excluding articles presented within the flow chart.

The analysis of TCS system literature categorised research according to the classifications proposed in Figure 3: those investigations using chemical reaction (without sorption) and those with sorption as the basis. The fact that these two classifications involve similar mechanisms in many cases makes it difficult to distinguish clear differences and to sort out the literature based on clearly defined criteria [50]. However, an effort was made to classify the literature obtained from the search process detailed in Figure 6. Overall, the number of

documents categorised as chemical reaction obtained after the screening process was lower than the number of publications associated with sorption approaches.

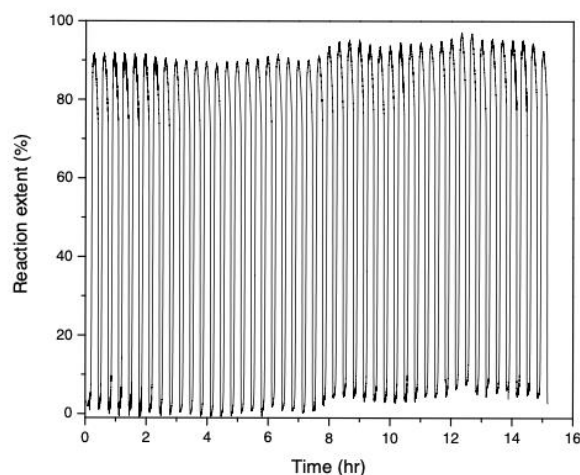
#### **4.1 Lithium in TCS. Chemical reactions**

Within the *chemical reaction* classification of TCS, it was possible to make two clear distinctions; lithium as working pair and lithium as doping agent. In Table 1, studies that have used lithium salts as the main functional compound or working pair are presented. The main lithium compounds used were LiOH [57], LiMnO<sub>2</sub> [58,59], and Li<sub>4</sub>SiO<sub>4</sub> [60]. Reactions were tested with different working pairs, for instance O<sub>2</sub> and CO<sub>2</sub> showing varied results [58,60]. Considering the data presented, it is possible to establish that lithium compounds have been used in redox reactions in order to produce hydrogen as an energy conversion technique. In this sense, Nakamura et al. [57] studied the reaction conditions of water-splitting through a Li system adopting a non-equilibrium process in order to control the entropy and to lower the reaction temperature. This system consists of three kinds of reactions, which are (i) hydrogen generation at 500 °C, (ii) Li generation through metal separation at 800 °C, and (iii) oxygen generation (hydrolysis reaction) by heating up to 300 °C. They demonstrated that the generation of H<sub>2</sub> below 800 °C by water-splitting using Li redox reactions was possible. However, some conditions in the reactions needed to be optimised in order to control the reaction cycles.

Lithium compounds have also been investigated in order to assess their possible application in thermochemical energy storage and in chemical heat pumps (CHP) at high temperature. Varsano [58] and Hlongwa [59] explored the possibility of utilising the reversible oxidation

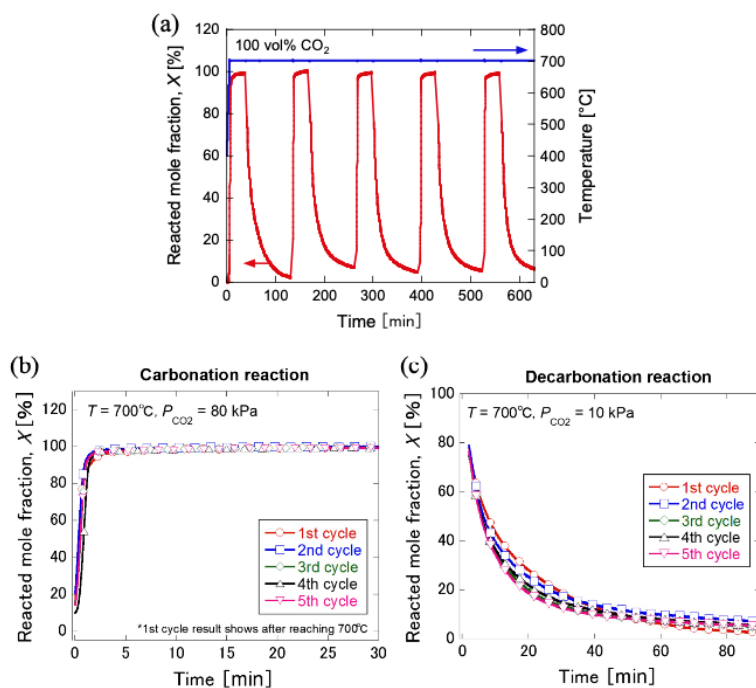


of lithium-manganese oxides as thermal energy storage at high temperature. The studies revealed that these reversible reactions are fast enough to store thermal energy between 800 – 1000 °C, with no deterioration detected when multiple redox cycles were performed (Figure 7), concluding that adding lithium to the conventional manganese oxide thermochemical cycle is highly favourable. Similarly, Takasu et al. [60] proposed the use of lithium orthosilicate/carbon dioxide ( $\text{Li}_4\text{SiO}_4/\text{CO}_2$ ) reaction system for applications in TCS and chemical heat pumps (CHP) at approximately 700 °C. In this TCS system, the decarbonation and carbonation were used for heat storage, and for heat output respectively. The results showed that  $\text{Li}_4\text{SiO}_4$  has a cyclic stability at 400 to 900 °C with no deterioration over 5 cycles and that the carbonation and decarbonation performance of  $\text{Li}_4\text{SiO}_4$  were sufficient for use as TCS material at around 700 °C (Figure 8). Furthermore, the results indicate that by regulating the  $\text{CO}_2$  pressure, the temperature for heat storage and heat output could be controlled.



**Figure 7.** Cyclical oxidation/reduction of  $\text{LiMnO}_2$  in the 800 – 1000 °C temperature range [58].

333



334

335 **Figure 8.** Durability of  $\text{Li}_4\text{SiO}_4$  reactivity observed at  $700^\circ\text{C}$ . (b) Comparison of carbonation  
336 and (c) decarbonation reaction [60].

337

338 **Table 1.** Lithium compounds used as working pair.

Lithium compound	Working pair	Reactions	$\Delta H$ [kJ/mol]	T [°C]	$q_v$ [kJ/L]	$q_g$ [kJ/kg]	References
LiOH	LiOH/Li	$2\text{LiOH(s)} + 2\text{Li(l)} \rightarrow 2\text{Li}_2\text{O(s)} + \text{H}_2\text{(g)}$	-232	500	n.a	n.a	[57]
		$2\text{Li}_2\text{O(s)} \rightarrow \text{Li}_2\text{O}_2\text{(s)} + 2\text{Li(g)}$	883	800	n.a	n.a	
		$\text{Li}_2\text{O}_2\text{(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{LiOH(s)} + 1/2\text{O}_2\text{(g)}$	-51	300	n.a	n.a	
LiMnO <sub>2</sub>	LiMnO <sub>2</sub> /O <sub>2</sub>	$3\text{LiMnO}_2\text{(s)} + 1/2\text{O}_2\text{(g)}$	21(ox); 25(red)	800-1000	n.a	n.a	[58]

LiMnO <sub>2</sub>	LiMnO <sub>2</sub> /O <sub>2</sub>	$\leftrightarrow \text{Li}_2\text{MnO}_3(\text{s})$ $+ \text{LiMn}_2\text{O}_4(\text{s})$ $3\text{LiMnO}_2(\text{s}) + 1/2\text{O}_2(\text{g})$ $\leftrightarrow \text{Li}_2\text{MnO}_3(\text{s})$ $+ \text{LiMn}_2\text{O}_4(\text{s})$	37	700	n.a	n.a	[59]
Li <sub>4</sub> SiO <sub>4</sub>	Li <sub>4</sub> SiO <sub>4</sub> /CO <sub>2</sub>	$\text{Li}_4\text{SiO}_4(\text{s}) + \text{CO}_2(\text{g}) \leftrightarrow$ $\text{Li}_2\text{CO}_3(\text{s}) + \text{Li}_2\text{SiO}_3(\text{s})$	-94	650-700	750 <sup>†</sup>	780 <sup>†</sup>	[60]
				650-700	650 <sup>‡</sup>	670 <sup>‡</sup>	

339 Note: ΔH – Heat of reaction; T – temperature of reaction; q<sub>v</sub> – volumetric thermal energy  
340 density; q<sub>g</sub> – gravimetric thermal energy density; n.a. – not available. <sup>†</sup>used in TCS, <sup>‡</sup>used  
341 in chemical heat pump (CHP).

342

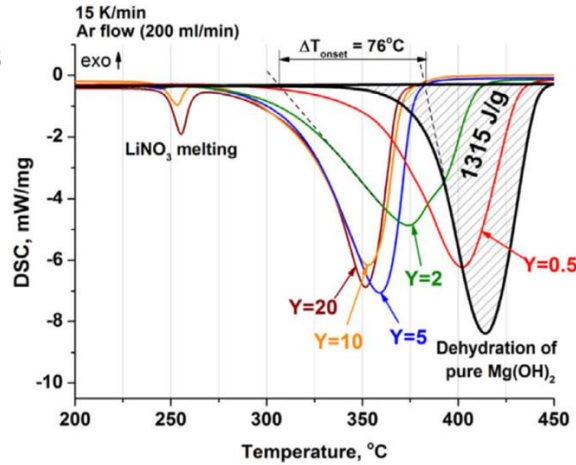
343 Lithium has not only been used as the main reactant component (i.e. working pair). In fact,  
344 there is a number of investigations in which lithium compounds can be also applied as an  
345 adjuvant or enhancer in the process of thermal storage, this has been frequently referred under  
346 the concept of *doping*. The doping effect of lithium helps to promote the thermal storage  
347 capacity of other working pairs (e.g. MgO and CaO) by changing the reaction kinetics. This  
348 effect includes the reduction of the dehydration barrier, decreasing the reaction temperature  
349 at which chemical bonds dissociate, for instance promoting the hydroxyl (OH<sup>-</sup>) bond-breaking  
350 from calcium hydroxide (Ca(OH)<sub>2</sub>) [61]. Additionally, lithium doping has been shown to  
351 promote the process of carbonation, an effect shown by Shkatulov et al. [62] where applying  
352 salts of lithium acetate (CH<sub>3</sub>COOLi) and lithium potassium nitrate (Li<sub>0.42</sub>K<sub>0.58</sub>NO<sub>3</sub>) increased  
353 the carbonation conversion, enhancing the process of heat storage.

354

355 The lithium salts used as dopants are listed in Table 2. As can be seen in the table, the main  
356 doping lithium-based salts are LiCl [63,64], LiOH [61,64], LiNO<sub>3</sub> [65,66], Li<sub>4</sub>SiO<sub>4</sub> [67] and

LiKNO<sub>3</sub> [62,68]. These salts have been used in multiple investigations, showing good thermal stability and expanding the applicability of the compounds as a heat storage materials. Several studies have been conducted in order to investigate the effect of the addition of lithium compounds to the dehydration and hydration reactions of different compounds. For instance, Yan and Zhao [61] investigated the micro-mechanism of CaO/Ca(OH)<sub>2</sub> heat storage system doped with Li and Mg. The results showed that the symmetry and the crystal structure of the transition state are altered after doping, reducing the energy barrier of the dehydration from Ca(OH)<sub>2</sub> to CaO from 0.40 eV (without doping) to 0.11 eV (with Li doping). They concluded that this reduction allows the same heat storage efficiency to be achieved at a lower temperature with Li doping. Ishitobi et al. [63], studied the effects of doping magnesium hydroxide with lithium chloride by evaluating several operational parameters such as mixing ratio, hydration temperature and water vapour pressure on the hydration performance. To do this, they employed lithium chloride to modify magnesium hydroxide as a TCM. The heat output density was found to be close to 1400 kJ/kg (Table 2), at a hydration temperature of 110 °C and water vapour pressure of 57.8 kPa. Due to this value being higher than the heat output density of pure magnesium hydroxide, the study suggested that the LiCl/MgO system can be used as a new material alternative for applications in TCS. Likewise, Shkatulov et al. [65], performed a dehydration study using magnesium hydroxide doped with lithium nitrate (LiNO<sub>3</sub>/Mg(OH)<sub>2</sub>·Y (where Y is the LiNO<sub>3</sub> content). The results indicate that lithium salt diminished the dehydration start temperature by 76 °C in the final material; while the reaction heat remained almost unaffected below 5 wt.% of lithium salt content. The LiNO<sub>3</sub>-doped Mg(OH)<sub>2</sub> was able to store up to 800 – 1000 kJ/kg at a temperature below 235 °C (with a water vapour pressure of 2.3 kPa). The position

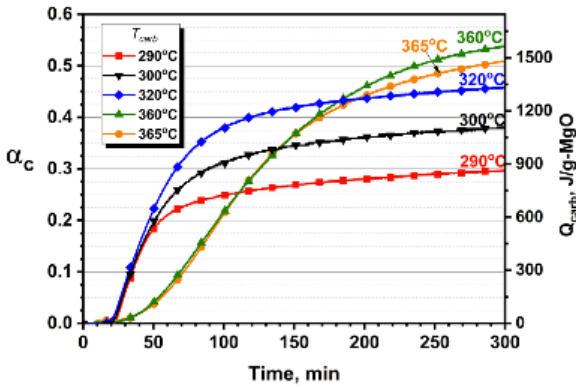
of the dehydration peak depends on Y: the higher the Li salt content, the lower the peak temperature (Figure 9).



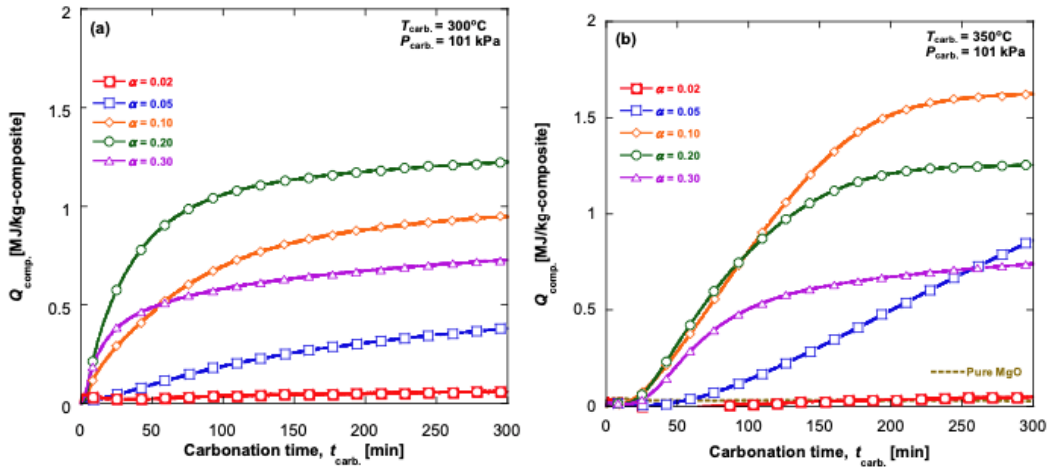
**Figure 9.** DSC-curves and the dehydration temperature of  $\text{LiNO}_3/\text{Mg(OH)}_2 \cdot Y$  [65].

Similarly, lithium compounds have also been used to study the effect of doping in carbonation/decarbonation reactions. Skatulov et al. [62] adapted the  $\text{MgO}/\text{CO}_2$  working pair to promote the TCS dynamics at medium temperatures, studying the carbonation kinetics of  $\text{Li}_{0.42}\text{K}_{0.58}\text{NO}_3/\text{MgO}$ , the de-carbonation kinetics of  $\text{Li}_{0.42}\text{K}_{0.58}\text{NO}_3/\text{MgCO}_3$  and the cycling stability of the composite. The work demonstrated that the de-carbonation process can be carried out at  $T > 330^\circ\text{C}$ , and that the heat storage capacity of the doped salt  $\text{MgO}$  was estimated to be 1600 kJ/L, concluding that these parameters are promising for TCS (Figure 10). In the same way, Kim et al. [68] adapted the  $\text{MgO}/\text{CO}_2$  working pair to study the effect of doping with  $(\text{LiK})\text{NO}_3$ . To do this, a number of carbonation dynamic experiments were carried out. The results showed that at  $T_{\text{carb}}$  of  $350^\circ\text{C}$ , the optimal salt content suggested was  $\alpha = 0.20$  so as to ensure a high and stable  $Q_{\text{comp}}$  with values of 1180 – 1250 kJ/kg-composite

in the temperature range 290 - 350 °C (Figure 11). Overall and as it has been illustrated throughout this section, several lithium salts are promising compounds to enhance the functionality and range of application of heat storage systems.



**Figure 10.** Carbonation kinetics of (LiK)NO<sub>3</sub>/MgO [62].



**Figure 11.** Specific useful heat,  $Q_{comp.}$ , as a function of the carbonation time at (a) 300 °C and (b) 350 °C [68].

**Table 2.** Lithium compounds used as doping element.

Lithium compound	Working pair	Reactions	$\Delta H$ [kJ/mol]	T [°C]	$Q_{total}$ [kJ/kg]	$q_v$ [kJ/L]	$q_g$ [kJ/kg]	$p$ [kPa]	Energy barrier [eV]	References
LiCl	MgO/H <sub>2</sub> O	MgO(s) + H <sub>2</sub> O(g) $\leftrightarrow$ Mg(OH) <sub>2</sub> (s)	-81	300 (dehydration) 110-200 (hydration)	1400 (100°C) 724 (180°C)	n.a	n.a	57.8 (H <sub>2</sub> O)	n.a	[63]
LiOH · H <sub>2</sub> O	CaO/H <sub>2</sub> O	CaO(s) + H <sub>2</sub> O(g) $\leftrightarrow$ Ca(OH) <sub>2</sub> (s)	109.3	430 (dehydration)	n.a	n.a	n.a	n.a	0.11	[61]
Li <sub>4</sub> SiO <sub>4</sub>	Li <sub>4</sub> SiO <sub>4</sub> /CO <sub>2</sub>	Li <sub>4</sub> SiO <sub>4</sub> (s) + CO <sub>2</sub> (g) $\leftrightarrow$ Li <sub>2</sub> CO <sub>3</sub> (s) + Li <sub>2</sub> SiO <sub>3</sub> (s)	-94	800	n.a	510	n.a	100 (carbonation, CO <sub>2</sub> ) 5 (decarbonation, CO <sub>2</sub> )	n.a	[67]
LiNO <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) $\leftrightarrow$ MgO(s) + H <sub>2</sub> O(g)	81	<235 (dehydration)	800-1000	n.a	n.a	2.3 (H <sub>2</sub> O)	n.a	[65]
LiNO <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) $\leftrightarrow$ MgO(s) + H <sub>2</sub> O(g)	81	90-150 (hydration)	290-1024	n.a	n.a	16.7-33.5 (H <sub>2</sub> O)	n.a	[66]
LiKN O <sub>3</sub> CH <sub>3</sub> COOLi	MgO/CO <sub>2</sub>	MgCO <sub>3</sub> (s) $\leftrightarrow$ MgO(s) + CO <sub>2</sub> (g)	116.4	>330 (decarbonation) 280-360 (carbonation)	n.a	1600	1600	0-100 (CO <sub>2</sub> )	n.a	[62]
LiKN O <sub>3</sub>	MgO/CO <sub>2</sub>	MgO(s) + CO <sub>2</sub> (g) $\leftrightarrow$	-116.4	~400 (carbonation)	1180-1250	n.a	n.a	50–101 (CO <sub>2</sub> )	n.a	[68]

			MgCO <sub>3</sub> (s)		300-350 (decarb onation)					
LiCl	CaO/	CaO(s)	-	350	450-	n.a	n.a	7.4	n.a	[64]
LiOH	H <sub>2</sub> O	+	104.	(dehydr	670			(H <sub>2</sub> O)		
Li <sub>2</sub> C		H <sub>2</sub> O(g)	4	ation)						
O <sub>3</sub>		↔Ca(O		110						
		H) <sub>2</sub> (s)		(hydrati						
				on)						

Note:  $\Delta H$  – Heat of reaction;  $T$  – temperature of reaction;  $Q_{total}$  – heat output density;  $q_v$  – volumetric thermal energy density;  $q_g$  – gravimetric thermal energy density;  $p$  – pressure; n.a. – not available.

Within the chemical reaction classification, lithium compounds have been used as a working pair in: i) redox reaction to produce hydrogen as an energy conversion technique in order to control the entropy and to lower the reaction temperature of the system, and ii) in chemical heat pumps at high temperature to improve the performance of the system favouring the thermochemical cycles. Lithium compounds are also used as doping agents to modify the reaction conditions of other pure salts in: i) dehydration and hydration reactions to reduce both the energy barrier and temperature of the reaction, unchanging the reaction heat and increasing the heat output density, ii) carbonation/decarbonation reactions to promote TCS dynamics with high and stable storage densities. Overall, in this section by applying the aforementioned screening approach it was possible to only retrieve a limited number of documents – 12 research documents in total –, making it challenging to determine a specific trend in the use of working pairs or doping based on lithium salts.



## **4.2 Lithium in TCS. Sorption**

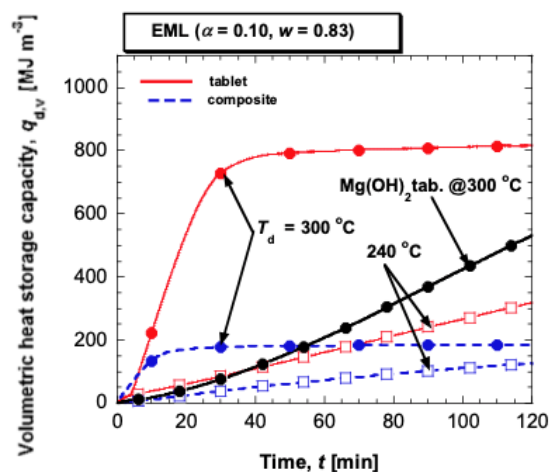
As expressed previously, sorption is a mechanistic approach part of the TCS systems. Such mechanisms involve the physical interaction between a sorbent and a sorbate. The sorbate molecules can interact with the bulk of a solid or liquid that acts as sorbent (i.e. absorption) and similarly, sorbate molecules can interact with the surface of a solid or liquid that also act as sorbent (i.e. adsorption). Independently of the specific mechanisms involved in the sorption process, such processes will take in and release energy. The modification of the compounds used as reactants (i.e. sorbate and sorbent) and the condition of the process (i.e. temperature, pressure, surface area/ratio, salt content amongst other things) will enable to the application of this technology under different conditions depending on the intended function.

Sorbent materials are often evaluated by measuring the thermal conductivity, and heat storage capacity. These parameters will indicate the heat and mass transfer performance of the system. The result of literature screening is shown in Table 3. As it can be seen, the sorption technologies listed usually involve the application of composite materials, salt in porous matrix (CSPMs), as the sorbent. The application of composites is one approach used to improve the sorption kinetic performance. The composites incorporate materials that form a matrix to contain the salt and enhance cycle stability, thermal conductivity, and promote the heat and mass transfer. For instance, common composites using lithium salts are; activated carbon (AC) mixed with expanded natural graphite treated with sulfuric acid (ENG-TSA) [69,70], expanded graphite (EG) [71–73], activated alumina (AA) [74], expanded vermiculite (EVM) [75], Wakkanai siliceous shale (WSS) [76], silica gel (SG) [77], vermiculite (VM)

[78–80], silica-alumina (S-AA) [81], zeolite (13X-Z, NaY-Z, Z) [82–85], graphene oxide (GO) [86]. In this sense Yu et al. [69,70] developed a new type of consolidated composite sorbent using activated carbon (AC) as the porous matrix to harbour the LiCl salt. Besides, this new composite was further mixed with expanded natural graphite, and treated with sulfuric acid (ENG-TSA) to increase heat transfer. Additionally, silica solution (SS) was also included in the matrix as a binder to enhance mechanical strength. Then, the results were compared against a more standard silica gel-LiCl composite sorbent. The analysis showed that activated carbon is a better choice of porous matrix compared with silica gel, reaching a water uptake up to 0.97 g/g at a temperature of 30 °C and pressure of 1.66 kPa. The study also showed that sorbent with lower bulk densities had a better performance regarding its kinetics (unit mass), due to a better water transport in loose sorbents. They proved that their composite could be a possible solution for TES systems using LiCl/H<sub>2</sub>O as the working pair. Because of these results, Yu et al. subsequently investigated sorption thermal energy storage using a 1 kWh lab-scale sorption prototype [70]. The results indicated that the whole experiment collected sorption heat about 1496 kJ, achieving 80% of the predicted target of 1869 kJ.

Lithium compounds have also been used in conjunction with expanded graphite (EG) as porous matrix, which not only increases the thermal conductivity of the pure salt by a factor of 5-10, but also acts as a porous carrier structure that prevents the agglomeration of particles of pure salt. Thus, Zhao et al. [71], developed and investigated a 10 kWh short-term sorption TES device. To do this, they used composite sorbent made from LiCl with the addition of EG. The results revealed that under experimental conditions (Table 3), the heat storage capacity reached values of 10.25 kWh, of which the heat of sorption represents approximately

60%. Furthermore, the heat storage density obtained was 65.29 kWh/m<sup>3</sup> of composite sorbent. In the same way, Li et al. [72], developed a form-stable LiOH/EG composite and the thermochemical performance was investigated. They demonstrated that the sample with 8 wt.% EG-doped was the most promising, with a thermal conductivity of 6.92 W/(m K) and energy density of 1120 kJ/kg. Similarly, Myagmarjav et al. [73], developed a novel candidate material denoted EML, this material was obtained by mixing pure Mg(OH)<sub>2</sub> with EG and LiBr. The EML composite developed was then compressed in order to obtain EML tablets and thus achieve higher energy densities. The results showed that the EML tablets could store heat of 815.4 MJ/m<sup>3</sup>(tablet) at 300 °C during 120 min, which is almost 4.4 times higher than the EML composite under the same experimental conditions (Figure 12).



**Figure 12.** Volumetric heat storage capacities of the EML tablet and composite [73].

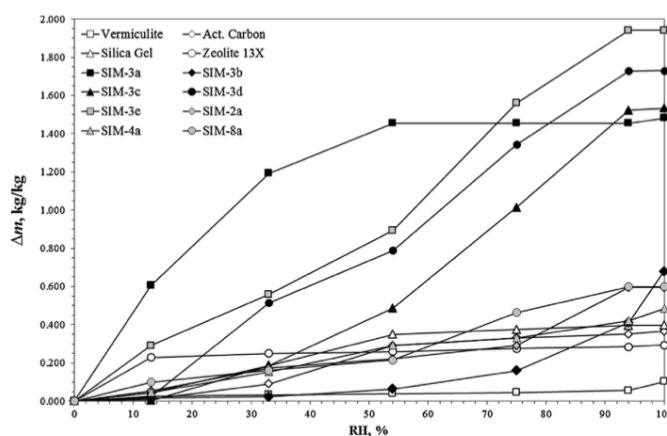
Composite materials using LiCl, LiNO<sub>3</sub>, LiBr and vermiculite (VM) as a host matrix have been investigated since this matrix compound has been shown to meet the main requirements for an inert matrix upon which the salt can be deposited. Therefore, Zhang et al. [75],

developed a novel composite sorbent by impregnating LiCl into expanded vermiculite (EVM) to store low-temperature heat below 100 °C. They indicated that the sample EVLiCl20 (with a salt content of 32.60%, and water uptake of 1.41 g/g) was the optimal composite sorbent, reaching a mass energy storage density of 1.21 kWh/g, and volume energy storage density of 171.61 kWh/m<sup>3</sup>. In general, LiCl salts inserted into EVM showed better performance in relation to water uptake, mass energy storage density, and volume energy storage density compared to other salt tested, such as XX, YY.~~since all of these properties increase with salt content.~~

Vermiculite has also been assessed using other lithium salts. Casey et al. [78] evaluated the selection of hygroscopic salts and desiccant matrices as candidate materials for open thermal energy storage. Candidate materials selected were silica gel (SG), zeolite (Z), activated carbon (AC) and vermiculite (VM) as matrices, and CaCl<sub>2</sub>, MgSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>3</sub> and LiBr as salts. The N<sub>2</sub> physisorption analysis indicated that in the non-vermiculite matrices, some damage may have occurred within the pore structure. On the other hand, all samples using vermiculite SIM-3a (CaCl<sub>2</sub>-VM), SIM-3c (Ca(NO<sub>3</sub>)<sub>2</sub>-VM) and SIM-3e (LiBr-VM) showed promising values of moisture vapour sorption isotherms with EMC values up to 1.9 kg/kg (Figure 13). However, sample SIM-3c (Ca(NO<sub>3</sub>)<sub>2</sub>-VM) was discarded because it showed an abrupt reduction in the potential performance because of its large T<sub>emp</sub> response time. Finally, the study concluded that the samples SIM-3a (CaCl<sub>2</sub>-VM), and SIM-3e (LiBr-VM) demonstrated a very good potential to be used in an open TES system.

In a different approach, Sutton et al. [79] studied the hydration/dehydration of inorganic salts using CaCl<sub>2</sub> and LiNO<sub>3</sub> impregnated into porous vermiculite (VM). The study performed at

high packing density showed that (during discharge cycle) the performance of the two SIM materials (salt in matrix) was significantly lower than that expected. However, when Sutton et al. [80] studied the interactions between common SIMs (salt in matrices) using  $\text{CaCl}_2$ ,  $\text{LiNO}_3$ ,  $\text{MgSO}_4$  and vermiculite by using layering and blending techniques, the results showed that layering the  $\text{CaCl}_2$  on the  $\text{LiNO}_3$  gave a more efficient thermal release strategy and reached a thermal storage density of  $0.2 \text{ GJ/m}^3$ . This research also emphasised that a significant reduction in efficiency may be due to an improper mixing of the material.

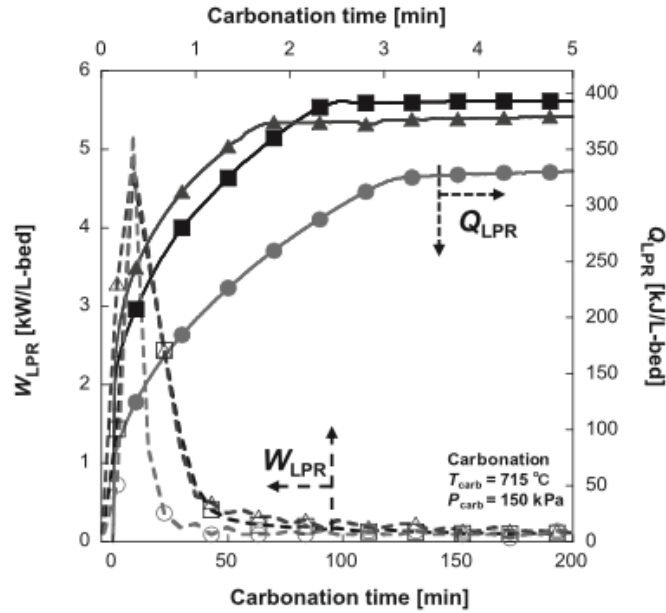


**Figure 13.** Moisture vapour sorption isotherms for all candidate materials [78].

Lithium salts can also be improved for TCS applications in order to enhance the hydration properties of the materials, generating a reduction in the apparent activation energy of the thermochemical reaction process. Li et al. [82] synthesised lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) by impregnation method with hygroscopic materials (where polyethylene glycol (PEG), lithium chloride  $\text{LiCl}$ , 13X-zeolite (13X-Z) and NaY-zeolite (NaY-Z) were chosen as hydrophilic promoters). The results revealed that  $\text{LiOH} \cdot \text{H}_2\text{O}/13\text{X-Z}$  presented the lowest apparent activation energy ( $21.5 \text{ kJ/mol}$ ) and the highest heat storage density  $1949$

kJ/kg (3 times higher than the pure LiOH). In a different research, Kim et al. [83], studied the reaction of  $\text{Li}_4\text{SiO}_4/\text{CO}_2$  for recovery and utilisation of the high-temperature produced from industrial processes. To do this, two reactors ( $\text{Li}_4\text{SiO}_4/\text{CO}_2$  packed bed reactor (LRP) and zeolite packed bed reactor (ZPR)) were developed as TES. The carbonation process (thermal energy output) was carried out at 715 °C and 150 kPa of  $\text{CO}_2$  pressure conditions, and the decarbonation process (thermal energy storage) was performed using pressure difference between the two beds (i.e. LRP and ZPR). The analysis showed thermal energy output density of LRP around 331 – 395 kJ/L-packed bed, and 759 – 904 kJ/L-material (Figure 14). The proposed  $\text{Li}_4\text{SiO}_4/\text{CO}_2$ /zeolite TCS system was shown to be able to improve the efficiency of the high-temperature industrial processes.

In an attempt to further characterise the effectiveness of  $\text{Li}_4\text{SiO}_4/\text{CO}_2$ /zeolite as a TCS system, Takasu et al. [84] and Kim et al. [85] tested the same  $\text{Li}_4\text{SiO}_4/\text{CO}_2$ /zeolite TCS system for high temperature performance. Takasu et al's [84] results indicated that carbonation of  $\text{Li}_4\text{SiO}_4$  was completed after 5 min, while decarbonation was completed after 150 min under isothermal experiments. In this case, the maximum  $w_{\text{out}}$  and  $w_{\text{in}}$  rates of  $\text{Li}_4\text{SiO}_4$  with 59% of porosity, were 7.2 kW/kg and 1.9 kW/kg, respectively. Meanwhile, Kim et al. [85] additionally developed tablet forms of  $\text{Li}_4\text{SiO}_4$  named K-tablets. The K-tablet showed a maximum thermal energy output rate of 9.82 kW/kg-tablet under 650 °C on the 10<sup>th</sup> cycle. Whilst, the thermal energy output rate for the pure powder was 3.25 kW/kg-  $\text{Li}_4\text{SiO}_4$  under the same reaction temperature.



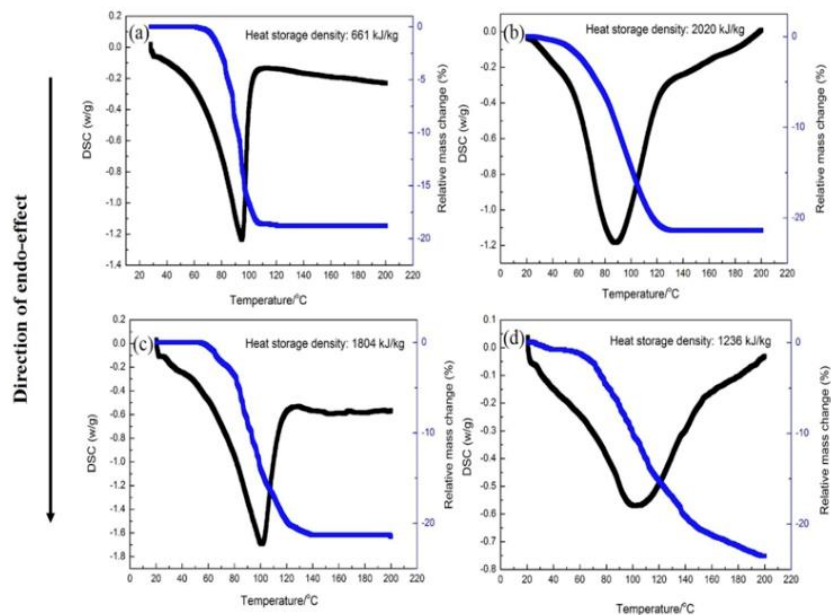
**Figure 14.** Thermal energy output capacity and output rate for LPR bed [83].

In order to expand the number of TCS applications, a comparative performance study for low-temperature TCS with  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$ /graphene oxide (GO) was performed by Yang et al. [86]. Pure  $\text{LiOH} \cdot \text{H}_2\text{O}$  showed an endothermic heat about 1460 kJ/kg at 65 °C, with dehydration starting at around 60 °C and finishing at 98 °C. Nonetheless,  $\text{LiOH}$  reacted with water vapour very slowly (35% even after 1 h, with 511 kJ/kg). Thus, the enhancement of hydration rate of  $\text{LiOH}$  is required for practical application. In this regard,  $\text{LiOH} \cdot \text{H}_2\text{O}$  nanoparticles (27.1 wt.%) supported on graphene oxide (GO) obtained high heat storage density (1980 kJ/kg), due to the increase in surface area of nanoparticles in contact with the water molecules.

A relatively new technology to improve the energy storage capacity of TCS based on sorption has been the engineering of nanomaterials. Nanomaterials, for instance nanotubes and nanospheres, are an alternative for production of matrix materials since they exhibit large

surface area, high thermal conductivity, low bulk density and chemical stability. The work done by Grekova [87] and Yang et al. [88] are good examples of the applications of carbon nanotubes (CNTs) and carbon nanospheres (CNSs) respectively. Grekova et al. [87] investigated novel composite sorbents based on multi-wall carbon nanotubes (MWCNTs) impregnated with LiCl and LiBr for TCS, employing water and methanol as sorbates. The results showed that the methanol sorption capacity of LiCl/MWCNT and LiBr/MWCNT reaches 1.65 g/g and 0.9 g/g respectively. The crystalline hydrates,  $\text{LiCl} \cdot \text{H}_2\text{O}$  and  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ , were formed due to water sorption on the LiCl-based composites. The water sorption capacity for the both systems exceeded 1g/g, which is favourable for TCS. The heat storage capacity of LiCl/MWCNT under experimental conditions and the cycles applied reached 1.6 and 1.7 kJ/g (or 445 and 470 Wh/kg) with methanol and water respectively, exceeding equivalent values for common and innovative adsorbents suggested for sorption thermal energy storage (STES). This demonstrates the great potential of the new lithium salts composites for STES which encourages a wider implementation of this emerging technology. In the same way, Yang et al. [88] studied the effect of carbon nanoadditives on  $\text{LiOH} \cdot \text{H}_2\text{O}$ -based composite for low temperature TCS. In this approach, carbon nanospheres (CNSs) and multi-walled carbon nanotubes (MWCNTs) were used to modify  $\text{LiOH} \cdot \text{H}_2\text{O}$ . The results revealed that the hydration reaction rates of the composite materials were improved reaching heat storage densities of 2020 and 1804 kJ/kg for  $\text{LiOH} \cdot \text{H}_2\text{O}$ /CNSs and  $\text{LiOH} \cdot \text{H}_2\text{O}$ /MWCNTs respectively (Figure 15). The study concluded that a certain enhancement of the thermal conductivity of the composite TCM is observed as a consequence of the additives used in the investigation.





**Figure 15.** TG-DSC curves of as-synthesized samples: (a) LiOH pure, (b) LiOH/CNSs, (c) LiOH/MWCNTs, and (d) LiOH/AC after 1 h of hydration [88].

The results shown in Table 3 evidence that sorption applications are frequently related to the utilisation of a solid matrix associated with other materials forming a composite. Even though single salts can be utilised as solid matrix, they usually fail because of the degradation, agglomeration and low thermal conductivity amongst other things. Thus, the application of composites has served as a general strategy to make it possible for salts that have previously exhibited challenging properties to be applied in such systems. Bearing this in mind, the same composite strategy has become the target for further technical improvements.

606 **Table 3.** Lithium compound used in sorption applications.

Working pair																
Lithium compound	Sorbate	Porous matrix	Li content [%]	Sorbate uptake [g/g]	T [°C]	<i>p</i> [kPa]	$\lambda$ [W/m K]	$K_p \times 10^{-12}$ [m <sup>2</sup> ]	<i>q</i> [kW]	$\varepsilon$	Recovered heat [kJ]	Heat storage density [kJ/kg]	Heat storage density [MJ/m <sup>3</sup> ]	Heat storage capacity [kWh]	Efficiency [%]	Reference
LiCl	H <sub>2</sub> O	AC mixed with ENG-TSA and SS	40	0.97	30	1.66	2.0 – 2.83	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	[69]
LiCl	H <sub>2</sub> O	AC mixed with ENG-TSA and SS	40	0.52	85(ch a); 40(dis )	n.a	2.6	3.43	0.86	0.7	2517	874 (consolidated sorbent) 2622 (LiCl)	n.a	n.a	93	[70]
LiCl	H <sub>2</sub> O	EG	n.a	n.a	85(ch a); 40(dis )	0.87-1.68	2.25	4.65	6.50	0.705	n.a	2612	n.a	8.52	94	[71]
LiCl	H <sub>2</sub> O	AA	14.68	0.41	120 (cha)	n.a	0.37	n.a	n.a	0.29	n.a	1041.5	n.a	n.a	n.a	[74]

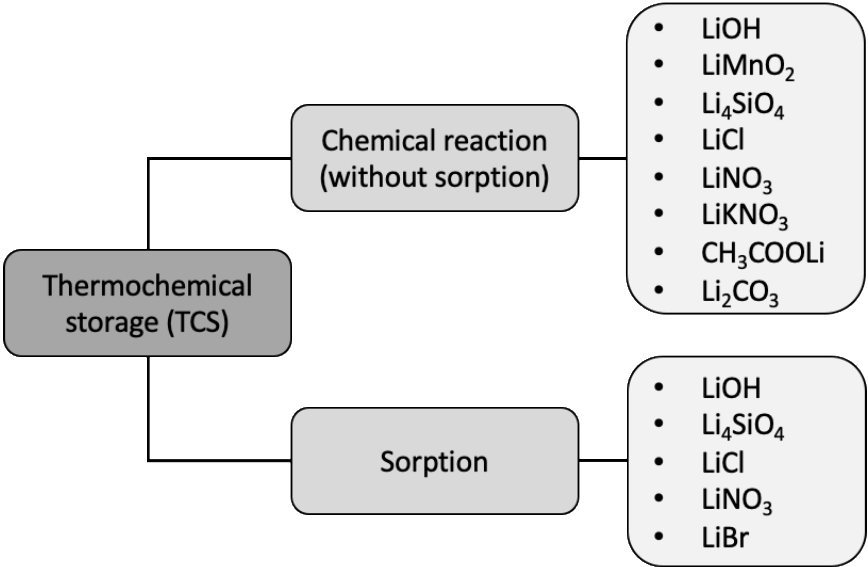
LiCl	H <sub>2</sub> O	EVM	32.60	1.41	<100	n.a	n.a	n.a	n.a	n.a	n.a	4356	n.a	n.a	n.a	[75]
LiCl	H <sub>2</sub> O	MWC NTs	41-42	0.09; 0.16; 0.26; 0.35; 0.52	75(ch a); 35(dis )	0.88(ad); 1.72(des)	n.a	n.a	n.a	n.a	n.a	1700	n.a	n.a	n.a	[89]
LiCl	H <sub>2</sub> O	WSS	9.6	0.6(a d); 0.1(des)	25-150	2.218	n.a	n.a	n.a	55	539.4(10 h); 327.1(4 h)	n.a	180	n.a	65.7(10 h); 39.8(4 h)	[76]
LiCl	H <sub>2</sub> O	MWC NTs	44	1.04	75(ch a); 35(dis )	0.9; 1.7; 3.2; 5.6	n.a	n.a	n.a	n.a	n.a	1700 (ST)	n.a	n.a	n.a	[87]
LiCl	CH <sub>3</sub> OH	MWC NTs	44	1.65	75(ch a); 35(dis )	7.3; 9.6; 12.7; 16.5; 21.3; 27.3	n.a	n.a	n.a	n.a	n.a	1600 (LT)	n.a	n.a	n.a	
LiCl	CH <sub>3</sub> OH	SG	20	0.4	34-53	n.a	n.a	n.a	5.4	n.a	n.a	620	n.a	n.a	n.a	[77]
LiBr	H <sub>2</sub> O	EG	10	n.a	300(c ha); 110(dis )	57.8	1.91	n.a	n.a	n.a	n.a	n.a	815.4	n.a	n.a	[73]
LiNO <sub>3</sub>	H <sub>2</sub> O	VM	24	n.a	<130(cha)	n.a	0.0659	n.a	n.a	n.a	n.a	286.9	n.a	n.a	n.a	[78]
LiBr <sup>*</sup>	H <sub>2</sub> O	VM	24	n.a	<130(cha)	n.a	0.0691	n.a	n.a	n.a	n.a	268.9	n.a	n.a	n.a	

LiNO <sub>3</sub>	H <sub>2</sub> O	VM	n.a	n.a	10-80	n.a	n.a	n.a	n.a	n.a	n.a	n.a	182	n.a	n.a	[79]
LiNO <sub>3</sub>	H <sub>2</sub> O	VM	n.a	n.a	80	n.a	n.a	n.a	n.a	n.a	n.a	n.a	200	n.a	n.a	[80]
LiNO <sub>3</sub>	H <sub>2</sub> O	S-AA	5.3; 10.2 ; 14.9	0.15; 0.18; 0.19	20- 150	n.a	n.a	n.a	n.a	n.a	n.a	n.a	273.6 ; 342; 334.8	n.a	n.a	[81]
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	Ni- CNTs	14*; 23; 39; 100	n.a	30- 120	2.97	3.7 8	n.a	n.a	n.a	n.a	3935	n.a	n.a	n.a	[90]
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	CNs	50	n.a	20- 120	2.97	1.9 5	n.a	n.a	n.a	n.a	2020	n.a	n.a	n.a	[88]
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	MWC NTs	50	n.a	20- 120	2.97	1.7 5	n.a	n.a	n.a	n.a	1804	n.a	n.a	n.a	
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	13X-Z	80	n.a	30- 200	2.98	n.a	n.a	n.a	n.a	n.a	1949	n.a	n.a	n.a	[82]
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	NaY- Z	80	n.a	30- 200	2.98	n.a	n.a	n.a	n.a	n.a	1624	n.a	n.a	n.a	
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	EG	85; 88; 92*; 95	0.64 1	105(c ha); 30(dis )	2.55	6.5 2	1. 2	n.a	0.6	n.a	1120	n.a	n.a	83.6	[72]
LiOH· H <sub>2</sub> O	H <sub>2</sub> O	GO	27.9	n.a	<200	2.55	1.8	n.a	n.a	n.a	n.a	1980	n.a	n.a	n.a	[86]
Li <sub>4</sub> SiO	CO <sub>2</sub>	Z	n.a	n.a	715	150	n.a	n.a	n.a	n.a	n.a	n.a	331- 395 (pack ed bed);	n.a	n.a	[83]

													759-904 (material)				
Li <sub>4</sub> SiO <sub>4</sub>	CO <sub>2</sub>	Z	n.a	n.a	700	100(char); 10(dec)	n.a	n.a	7.2 <sup>+</sup>	59	n.a	n.a	n.a	n.a	n.a	n.a	[84]
Li <sub>4</sub> SiO <sub>4</sub>	CO <sub>2</sub>	Z	n.a	n.a	~650	101(char); 0(dec)	n.a	n.a	>7 <sup>+</sup>	n.a	n.a	~450	n.a	n.a	n.a	n.a	[85]

607 Note: T – temperature of reaction; *p* – pressure;  $\lambda$  – thermal conductivity; *K<sub>p</sub>* – permeability; *q* – output power;  $\epsilon$  – sorbent porosity; AC  
608 – activated carbon; ENG-TSA – expanded natural graphite treated with sulfuric acid; SS – silica solutions; EG – expanded graphite; AA  
609 – alumina; S-AA – silica-alumina; EVM – expanded vermiculite; VM – vermiculite; Z – zeolite; SG – silica gel; GO – graphene oxide;  
610 Ni-CNTs – 3D-nickel-carbon nanotubes; CNs – carbon nanospheres; MWCNTs – multi-walled carbon nanotubes; WSS – wakkanai  
611 siliceous shale; cha – charge; dis – discharge; ad – adsorption; des – desorption; ST – short-term cycle; LT – long-term cycle; car –  
612 carbonation; dec – decarbonation; n.a. – not available. <sup>+</sup> - value reported as kW per gram; \* - parameter selected by the authors for further  
613 testing.

Figure 16 summarises the main lithium-containing salts applied in TCS systems based on chemical reactions and sorption mechanisms for heat storage.



**Figure 16.** Lithium-containing compounds used chemical reactions and sorption.

Within the sorption classification, the most common lithium salt applied in such systems was LiCl. When looking at LiCl, the most prevalent sorbate was water. For systems using LiCl/H<sub>2</sub>O, different types of matrices have been applied, however, activated carbon was the one showing the most outstanding results of all the other matrices tested, producing a thermal conductivity between 2.0 and 2.8 W/mK [69,70]. This value indicates the ability of the system to conduct and transfer heat. On the other hand, LiCl/H<sub>2</sub>O using EVM as the matrix reached a heat storage density of 4,356 kJ/kg [75]. In this case, this value indicates the amount of energy a system can store. It is important to stress the need to have a better and more standardised fashion of reporting the data so results can be compared more easily. In general, the combination of salts and sorbates tested tend to repeat throughout the analysed research,

however, the main variations are the harbouring matrices applied and the experimental setups. Overall, our screening rendered 22 research documents in total based on lithium salts.

## **5. Lithium compounds for TCS. A new look from patents**

From another point of view, the information available in patents is usually being misused, rather than being carefully considered to redirect and filter scientific research. A growing competitiveness and an economically critical description could be achieved by a thorough analysis of patented technologies and methods from research and development activities with industrial application, resulting in more businesses and higher economic rise with new products and processes, establishing renewed employments and protecting the environment and its resources [91]. In the context of technology management, the early detection of recent trends in technical improvement is of essential interest for investors and companies [92].

In this work, an exhaustive search was performed to analyse the patented inventions related to the use of lithium compounds for TCS applications; employing the WIPO website (<https://patentscope.wipo.int/search/es/search.jsf>), and filtering patents by applying the following Boolean: lithium AND thermal energy storage NOT battery\* NOT cell\*. Under these conditions, patents related to batteries or electrochemical cells were avoided, and only those patents mentioning thermal energy storage were included. In total, 25 patents were found related to thermochemical storage using lithium compounds. Amongst these, 23 patents are related to absorption (Table 4), where only LiBr units were proposed for absorption in TCS; and another two patents were based on chemical reactions. An important factor to consider is the energy source from which heat is obtained, results showed that since

2012 electric power is the main source proposed for refrigeration systems using a LiBr refrigeration unit, while the use of solar energy has been recently proposed. Moreover, a combination of both sources is gaining attention. Interestingly, all related patents for Li compounds in TCS were only requested and granted from one country; China.

The inventions using LiBr for absorption storage were categorised according to the energy source in electric power [93–101], industrial waste [102], solar energy [103–107] and mixed sources [108–115]. Several patents are related with the use of off-peak electricity and the safe aestivation [93,94,99,114], in this way energy consumption and costs are diminished. Many applications were proposed, the most significant were a carbonising system employed in the treatment of sludge and garbage [95], an energy supply system for hospitals [98], industrial waste heat recovery [102], an automotive solar energy [108] and a device applied to molten salt storage and linked to the technical field of solar-thermal power generation [115]. A path to optimise TES systems is blending different energy sources, such as solar energy with waste heat [111,115] or with electric power [113,114]. However, the most disruptive technology was a composite energy supply system, in which solar and geothermal energies are integrated, to exploit the complementary benefits of the two renewable energy sources and to improve the energy utilisation rate of the system. In fact, this system embodies a new concept for sustainable development of the environment [112].



**Table 4.** Patents related to the use of LiBr for refrigeration.

Energy source	Specifications	The invention	LiBr machine	Observations	Ref.
Electric power	Off-peak electricity	A thermal storage and energy accumulation conversion device	LiBr refrigerator	Stores energy by off-peak electricity, uses the energy at the high peak	[93]
	Steam power plant	A soil-source cold-storage heat accumulation system	The refrigeration unit in the refrigeration system can be driven by thermal energy, such as a LiBr refrigeration unit	Hot peak regulation usefulness of steam power plant, to draw the heat that stores during winter	[94]
	Heat and electricity generators	A sludge and garbage carbonising system	LiBr refrigerating machine room	Can simultaneously provide combined cooling, heat and power for a city and treat sludge and garbage	[95]
	Electric heater	A cold and hot antithetical couplet of fused salt energy storage supplies device	LiBr absorption heat pump unit	Fused saltwater steam generator with parallelly connected respectively between the steam user have steam water heat exchanger	[96]
	Electrical output of gas turbine generator group	A cooling heating and power triple co-generation peak shaving system	The combined solar LiBr absorption air conditioning system		[97]
	Gas turbine	An energy supply system synthesises in hospital based on gas turbine	LiBr steam type refrigerating unit		[98]
	Off-peak electricity and aestivation	A device considering safe aestivation and electric power peak-load regulation of a thermal power air cooled condenser	A LiBr unit	For solving the problem of safe aestivation of a thermal power air cooled unit.	[99]
	Internal combustion engine arrangement	An internal - combustion engine cylinder liner water cooling internal - combustion engine to admit air	Uses water as a refrigerant and a solution of LiBr as an absorbent for refrigeration	The cylinder liner water in the internal - combustion engine arrangement used as heat source for the LiBr units	[100]

	Gas engine	A heat and cold supply balance structure capable of stabilising the load of a gas turbine for a gas distributed energy station	LiBr absorption type refrigerating unit	Linked to the heat storage flash evaporation water tank through a LiBr heating steam pipeline	[101]
Industrial waste	Waste heat recovery from malt industry	A malt waste heat utilisation system of cooking with heat-retaining function	Organically combines heat pump energy conservation technology and solar photo-thermal technology		[102]
Solar energy	A solar thermal collector	A solar heating and refrigerating system	LiBr absorption refrigeration unit	A cooling water pump was employed	[103]
		An intelligent solar air-conditioning system	LiBr heat pump unit	Integrates the automatic control function, performs automatic intelligent control of heat collection and refrigeration by the microcomputer program according to the ambient temperature and the temperature of water	[104]
		A solar energy power generation light field system			[105]
		A solar double-effect absorption heat pump drying system with the thermal storage function		Hot wind is prepared by the LiBr unit for drying operation	[106]
	solar photo-thermal technologies	A combined solar LiBr absorption air conditioning system		It can have refrigerating, heat supply and hot water supply functions	[107]
	Solar energy (solar thermal energy steam type heat collector)	A solar thermal energy steam type refrigerating system		To satisfy ambient temperature requirements such as office space or operating control room	[108,109]
	Photo-thermal power generation	A device and method for performing distributed energy utilisation on			[110]

		molten salt stored energy and belongs to the technical field of photo-thermal power generation			
Mixed sources	solar energy and engine waste heat	An automotive solar energy and engine waste heat dual-energy refrigeration air conditioner		Uses solar energy and engine waste heat in automotive air conditioner	[111]
	Solar and geothermal energies	A solar photo-thermal system and ground source heat pump system coupled composite energy supply system		Complementation of advantages of the two renewable energy sources was achieved	[112]
	Solar energy and electric power (solar heat collector and a generator)	A combined energy-based solar LiBr absorption trigeneration system		Can reduce the instability of single energy supply, and can achieve cooling, heat supply, and hot water supply functions	[113]
	Solar, electric-thermal energies	A cooling and heating system, which provide multiple forms of energy to complement each other		Utilize solar water heating system and electric thermal storage boiler heating winter	[114]
	Solar energy, waste heat recovery and electrical power (solar heat collector, and an electricity storage power source)	A waste heat recovery type off-peak electricity energy storage heating system		Off-peak electricity and solar energy are used for recycling waste heat of a thermal power plant, and the purpose of saving energy is achieved	[115]

Finally, the only two detected patents related to TCS by chemical reactions, inventors employed lithium hydride (LiH) and proposed two heat energy storage methods based on metal hydride. The system is based on a confined space supported by a metal organic framework material (MOF) in one work [116] and by a covalent organic framework material (COF) in the other method [117]. Both methods considered storage of the heat energy through decomposition of the LiH in the confined space at high temperature to produce Li and hydrogen. Therefore, the hydrogen was fed into the confined space through a guide pipe to carry out high-density storage on the hydrogen. The release of the stored energy occurs by suitably increasing the temperature of the hydrogen store materials and releasing it into the confined space containing the metal (Li) to initiate the metal hydride reversible reaction, and consequently to release a large amount of the heat energy. The proposed storage methods have potential in industries such as CSP plants, nuclear power plants peak load shifting and waste heat recovery [116,117].

## **6. Future trends. Proposed Li material for TCS**

### **6.1 Technological and economic challenges**

The abundance of different strategies of TCS based on sorption technologies certainly indicates the potential of such approaches to be applied and tested in large-scale systems. The study and reduction of technical drawbacks such as parasitic sensible heating losses, cycle stability and system lifetime, partial charge/discharge requirements, complex system management, safety restriction around pressure vessels, potential toxicity of material, amongst others, will make possible the commercialisation of technology. Such technology

can be deployed for industrial and social activities so waste heat can be recovered and reused with limited energy waste generation.

Current and futures trends targeted at improving TCS materials are effectively looking at the nanoscale. Hence, changes in the nano-structures of the harbouring matrices have proven to be an efficient strategy to facilitate and enhance the heat storage capacity of TCS systems [REF]. As it has been demonstrated that the application of matrices improves the conductivity and permeability of a system, helps to stabilise the salt, and enhances its properties. The search for new matrices and novel strategies for their application will certainly need to consider aspects related to storage density. By managing the matrix properties it is possible to promote the sorbate's access to the salt. Some of these properties are i) matrix density, ii) salt content –how much salt can be held by the harbouring matrix–, iii) the surface/area of the salt –parameter that can be improved by reducing salt agglomeration –, iv) lifetime of the matrix – performance maintenance by avoiding the system's degradation overtime. For instance, in more complex devices such as heat-pumps or refrigeration, the application of matrix materials has been crucial to keep improving aspects related to performance, especially related to the capacity of a system to transfer heat in and out (i.e. thermal conductivity) and ways of improving the lifetime – number of cycles – of such units. These aspects will ultimately have an impact in the cost associated with the implementation of such technology.

When specifically looking at energy storage, an important factor to consider in TCS systems will be the energy density. This key metric is essential to establish the energy performance and to determine the energy storage capacity of a given system. As has been explained

throughout this review, the functional component of TCS systems are salts with sufficient capacity to store energy. The challenges of working with salts are to address variables related with i) reaction enthalpies, ii) activation energy, iii) temperature of reaction and iv) energy density. In some cases, these variables are not always compatible with a wide range of application of TCS systems. For instance, some salts can have high energy density – a usually desirable property – with a high temperature of reaction, which means that their application is limited to systems with a temperature high enough to reach the activation point (i.e. activation energy). Some alternatives to take advantage of such salts with high energy density, is by doping these salts. As explained in previous sections, the addition of a doping element can help to tune the temperature of reaction whilst maintaining the energy density of some particular salt. The application of different lithium salts has shown to be an alternative to improve the application of TCS systems at a broader range of reaction temperatures.

One important aspect that needs to be urgently addressed for TCS systems to reach full applicability is the high-cost of their implementation, specially associated with the (limited) availability of components in high demand, such as lithium salts. The high value of salts is mainly associated with the purification of the targeted elements and the complexity of the mixture [REF]. In this context, by-products and wastes from the mining industry represent an inexpensive (low-cost) source of materials for potential application in TCS systems. For instance, lithium carnallite ( $\text{LiCl} \cdot \text{MgCl}_2 \cdot 7\text{H}_2\text{O}$ ), a waste of Li-based compounds resulting from the copper-mining production process, does not have any current applications and must be stockpiled as residues. Therefore, the potential applications of lithium carnallite as TCS materials, would not only monetize these salts but also contribute to the reduction of the

accumulation of waste. Nonetheless, recent studies proved that this type of salt shows an ambiguous behaviour, presenting phase change and weight loss (decomposition) simultaneously at low temperature (temperature range 0 – 100°C [Milián2020]) which certainly hampers potential applications as TCS systems [Gutierrez2017]. Additionally, complex residual salts represent an extra challenge in terms of the consistency of the components of the mixture, which affects their performance in TCS applications. Hence, further improvements are required for these low-cost salts to be utilised in such systems

## **6.2 Environmental challenges**

As stated above, by-products and wastes from mining industries could be considered a potential source of active TCM compounds for TCS systems, which will give utility and economic value to material currently regarded as waste. The opportunity to find new applications for waste not only represents an additional economic value but also a strategy to reduce the environmental impacts that the accumulation of such waste could produce in the surrounding environment. It is important to stress that the mining activity of lithium has been under pressure to provide materials for electrochemical storage systems required by the transition to electric vehicles and the growing reliance on variable renewable energy generation. Such increase in lithium-based products has consequently increased the size and number of lithium extraction sites, activity that inherently has environmental impacts. This environmental duality is a signal in order to look for different strategies, and thus wastes and synthetic materials could potentially serve as a way to overcome unwanted environmental externalities.

771

772 The potential of TCS systems effectively represents an attractive mechanism for the  
773 reduction of energy losses and consequently, the reduction of the environmental stress  
774 derived from the process of energy generation. The current climate emergency calls to  
775 strengthen the efforts of the scientific community to have more and better alternatives for  
776 more energy-efficient technologies and to aim at the reduction of the impact of industries and  
777 other human activities upon the environment.

778

## 779 **7. Conclusions**

780

781 The expanding interest in having more diverse energy strategies has encouraged the  
782 development of several technologies associated with the production, storing and saving of  
783 energy. In this sense, the recovery of waste energy – energy losses from other industrial or  
784 social activities– has been investigated from different angles. The capacity of engineered  
785 chemical systems has proven to be an approach for energy storage. This study has aimed to  
786 determine the current state of the investigations and technological advances of TES using  
787 lithium as part of the system.

788 Thus, using a semiautomated screening approach from scientific databases we were able to  
789 evidence the following:

790

- 791 ○ Scientific research on TCS systems based on chemical reactions are less abundant  
792 than sorption systems under the methodology applied.
- 793 ○ The majority of studies analysed were TCS systems based on sorption.



- The TCS based on chemical reactions analysed in this review mostly apply lithium as a secondary component, often referred to as a dopant. Doping with lithium salts is used to change the activation energy and temperature of the reactions.
- The TCS research papers based on sorption primarily used LiCl/H<sub>2</sub>O and LiOH/H<sub>2</sub>O as the working pair. The salts were contained in a variety of different matrix materials that can exhibit highly variable properties.
- The commercial patents for TCS based on lithium were found to be mostly based on sorption technologies, where LiBr was the most common compound, used for refrigeration systems. In contrast, the commercial patents for TCS based on chemical reactions were limited, being LiH mostly used as the energy storage system.

## **Acknowledgements**

Authors acknowledge to ANID/FONDAP N° 15110019, CONICYT/PCI/REDES N°170131 projects

This work was partially funded by the Ministerio de Ciencia, Innovación y Universidades de España (RTI2018-093849-B-C31 - MCIU/AEI/FEDER, UE) and by the Ministerio de Ciencia, Innovación y Universidades - Agencia Estatal de Investigación (AEI) (RED2018-102431-T). The author at the University of Lleida would like to thank the Catalan Government for the quality accreditation given to their research group GREiA (2017 SGR 1537). GREiA is a certified agent TECNIO in the category of technology developers from the Government of Catalonia. This work is partially supported by ICREA under the ICREA Academia programme.

## **References**

- 818 [1] Rodríguez D, Busco C, Flores R. Information technology within society's evolution.  
819 Technol Soc 2015;40:64–72. <https://doi.org/10.1016/j.techsoc.2014.08.006>.
- 820 [2] Valayer PJ, Vidal O, Wouters N, van Loosdrecht MCM. The full energy cost of  
821 avoiding CO<sub>2</sub>: A clean-energy booking provision for a vigorous energy transition. J  
822 Clean Prod 2019;237. <https://doi.org/10.1016/j.jclepro.2019.117820>.
- 823 [3] Zubi G, Dufo-López R, Carvalho M, Pasaoglu G. The lithium-ion battery: State of  
824 the art and future perspectives. Renew Sustain Energy Rev 2018;89:292–308.  
825 <https://doi.org/10.1016/j.rser.2018.03.002>.
- 826 [4] Fernández AG, Gomez-Vidal J, Oró E, Kruizenga A, Solé A, Cabeza LF.  
827 Mainstreaming commercial CSP systems: A technology review. Renew Energy  
828 2019;140:152–76. <https://doi.org/10.1016/j.renene.2019.03.049>.
- 829 [5] National Minerals Information Center U. Mineral Commodity Summaries 2010. n.d.
- 830 [6] National Minerals Information Center U. Mineral Commodity Summaries 2020. n.d.
- 831 [7] Cabeza LF, Gutierrez A, Barreneche C, Ushak S, Fernández ÁG, Inés Fernández A, et  
832 al. Lithium in thermal energy storage: A state-of-the-art review. Renew Sustain  
833 Energy Rev 2015;42:1106–12. <https://doi.org/10.1016/j.rser.2014.10.096>.
- 834 [8] Gasia J, Gutierrez A, Peiró G, Miró L, Grageda M, Ushak S, et al. Thermal  
835 performance evaluation of bischofite at pilot plant scale. Appl Energy  
836 2015;155:826–33. <https://doi.org/10.1016/j.apenergy.2015.06.042>.
- 837 [9] Ushak S, Gutierrez A, Galleguillos H, Fernandez AG, Cabeza LF, Grágeda M.  
838 Thermophysical characterization of a by-product from the non-metallic industry as  
839 inorganic PCM. Sol Energy Mater Sol Cells 2015;132:385–91.  
840 <https://doi.org/10.1016/j.solmat.2014.08.042>.
- 841 [10] Miró L, Gasia J, Cabeza LF. Thermal energy storage (TES) for industrial waste heat

- (IWH) recovery: A review. *Appl Energy* 2016;179:284–301.  
<https://doi.org/10.1016/j.apenergy.2016.06.147>.
- [11] Xu B, Li P, Chan C. Application of phase change materials for thermal energy storage in concentrated solar thermal power plants: A review to recent developments. *Appl Energy* 2015;160:286–307. <https://doi.org/10.1016/j.apenergy.2015.09.016>.
- [12] González-Roubaud E, Pérez-Osorio D, Prieto C. Review of commercial thermal energy storage in concentrated solar power plants: Steam vs. molten salts. *Renew Sustain Energy Rev* 2017;80:133–48. <https://doi.org/10.1016/j.rser.2017.05.084>.
- [13] Palacios A, Barreneche C, Navarro ME, Ding Y. Thermal energy storage technologies for concentrated solar power – A review from a materials perspective. *Renew Energy* 2020;156:1244–65. <https://doi.org/10.1016/j.renene.2019.10.127>.
- [14] Navarro L, de Gracia A, Colclough S, Browne M, McCormack SJ, Griffiths P, et al. Thermal energy storage in building integrated thermal systems: A review. Part 1. active storage systems. *Renew Energy* 2016;88:526–47.  
<https://doi.org/10.1016/j.renene.2015.11.040>.
- [15] Navarro L, de Gracia A, Niall D, Castell A, Browne M, McCormack SJ, et al. Thermal energy storage in building integrated thermal systems: A review. Part 2. Integration as passive system. *Renew Energy* 2016;85:1334–56.  
<https://doi.org/10.1016/j.renene.2015.06.064>.
- [16] Marin P, Saffari M, de Gracia A, Zhu X, Farid MM, Cabeza LF, et al. Energy savings due to the use of PCM for relocatable lightweight buildings passive heating and cooling in different weather conditions. *Energy Build* 2016;129:274–83.  
<https://doi.org/10.1016/j.enbuild.2016.08.007>.
- [17] Ushak S, Fernández AG, Grageda M. Using molten salts and other liquid sensible

storage media in thermal energy storage (TES) systems. *Adv. Therm. Energy Storage Syst. Methods Appl.*, Elsevier Inc.; 2015, p. 49–63.  
<https://doi.org/10.1533/9781782420965.1.49>.

[18] Sarbu I, Sebarchievici C. *Thermal Energy Storage. Sol. Heat. Cool. Syst.*, Elsevier; 2017, p. 99–138. <https://doi.org/10.1016/B978-0-12-811662-3.00004-9>.

[19] Abedin AH, Rosen MA. A Critical Review of Thermochemical Energy Storage Systems. *Open Renew Energy J* 2011;4:42–6.

[20] Bai Z, Liu Q, Gong L, Lei J. Application of a mid-/low-temperature solar thermochemical technology in the distributed energy system with cooling, heating and power production. *Appl Energy* 2019;253.  
<https://doi.org/10.1016/j.apenergy.2019.113491>.

[21] Weber R, Dorer V. Long-term heat storage with NaOH. *Vacuum* 2008;82:708–16.  
<https://doi.org/10.1016/j.vacuum.2007.10.018>.

[22] Lahmidi H, Maurant S, Goetz V. Definition, test and simulation of a thermochemical storage process adapted to solar thermal systems. *Sol Energy* 2006;80:883–93.  
<https://doi.org/10.1016/j.solener.2005.01.014>.

[23] Van essen M, Zondag HA, Schuitema R, Helden W, Rindt C. Materials for thermochemical storage: characterization of magnesium sulfate. *Proc Eurosun* 2008.

[24] Azpiazu MN, Morquillas JM, Vazquez A. Heat recovery from a thermal energy storage based on the  $\text{Ca}(\text{OH})_2/\text{CaO}$  cycle. *Appl Therm Eng* 2003;23:733–41.  
[https://doi.org/10.1016/S1359-4311\(03\)00015-2](https://doi.org/10.1016/S1359-4311(03)00015-2).

[25] Dizaji HB, Hosseini H. A review of material screening in pure and mixed-metal oxide thermochemical energy storage (TCES) systems for concentrated solar power (CSP) applications. *Renew Sustain Energy Rev* 2018;98:9–26.

890 <https://doi.org/10.1016/j.rser.2018.09.004>.

891 [26] Koohi-Fayegh S, Rosen MA. A review of energy storage types, applications and  
892 recent developments. *J Energy Storage* 2020;27.  
893 <https://doi.org/10.1016/j.est.2019.101047>.

894 [27] Liu D, Xin-Feng L, Bo L, Si-quan Z, Yan X. Progress in thermochemical energy  
895 storage for concentrated solar power: A review. *Int J Energy Res* 2018;42:4546–61.  
896 <https://doi.org/10.1002/er.4183>.

897 [28] Almendros-Ibáñez JA, Fernández-Torrijos M, Díaz-Heras M, Belmonte JF, Sobrino  
898 C. A review of solar thermal energy storage in beds of particles: Packed and  
899 fluidized beds. *Sol Energy* 2019;192:193–237.  
900 <https://doi.org/10.1016/j.solener.2018.05.047>.

901 [29] Ortiz C, Valverde JM, Chacartegui R, Perez-Maqueda LA, Giménez P. The  
902 Calcium-Looping (CaCO<sub>3</sub>/CaO) process for thermochemical energy storage in  
903 Concentrating Solar Power plants. *Renew Sustain Energy Rev* 2019;113.  
904 <https://doi.org/10.1016/j.rser.2019.109252>.

905 [30] Zsembinszki G, Sole A, Barreneche C, Prieto C, Fernández AI, Cabeza LF. Review  
906 of reactors with potential use in thermochemical energy storage in concentrated solar  
907 power plants. *Energies* 2018;11. <https://doi.org/10.3390/en11092358>.

908 [31] Chen X, Zhang Z, Qi C, Ling X, Peng H. State of the art on the high-temperature  
909 thermochemical energy storage systems. *Energy Convers Manag* 2018;177:792–815.  
910 <https://doi.org/10.1016/j.enconman.2018.10.011>.

911 [32] Sunku Prasad J, Muthukumar P, Desai F, Basu DN, Rahman MM. A critical review  
912 of high-temperature reversible thermochemical energy storage systems. *Appl Energy*  
913 2019;254. <https://doi.org/10.1016/j.apenergy.2019.113733>.

- 914 [33] Wu S, Zhou C, Doroodchi E, Nellore R, Moghtaderi B. A review on high-  
 915 temperature thermochemical energy storage based on metal oxides redox cycle.  
 916 Energy Convers Manag 2018;168:421–53.  
 917 <https://doi.org/10.1016/j.enconman.2018.05.017>.
- 918 [34] Farulla GA, Cellura M, Guarino F, Ferraro M. A review of thermochemical energy  
 919 storage systems for power grid support. Appl Sci 2020;10.  
 920 <https://doi.org/10.3390/app10093142>.
- 921 [35] Clark RJ, Mehrabadi A, Farid M. State of the art on salt hydrate thermochemical  
 922 energy storage systems for use in building applications. J Energy Storage 2020;27.  
 923 <https://doi.org/10.1016/j.est.2019.101145>.
- 924 [36] Yan Y, Wang K, Clough PT, Anthony EJ. Developments in calcium/chemical  
 925 looping and metal oxide redox cycles for high-temperature thermochemical energy  
 926 storage: A review. Fuel Process Technol 2020;199.  
 927 <https://doi.org/10.1016/j.fuproc.2019.106280>.
- 928 [37] Chen B, Kuznik F, Horgnies M, Johannes K, Morin V, Gengembre E.  
 929 Physicochemical properties of ettringite/meta-ettringite for thermal energy storage:  
 930 Review. Sol Energy Mater Sol Cells 2019;193:320–34.  
 931 <https://doi.org/10.1016/j.solmat.2018.12.013>.
- 932 [38] Fedunik-Hofman L, Bayon A, Donne SW. Kinetics of solid-gas reactions and their  
 933 application to carbonate looping systems. Energies 2019;12.  
 934 <https://doi.org/10.3390/en12152981>.
- 935 [39] Padamurthy A, Nandanavanam J, Rajagopalan P. Evaluation of reaction  
 936 characteristics of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O for thermochemical energy storage. Mater Today  
 937 Proc 2019;17:239–45.

- 938 [40] Yuan Y, Li Y, Zhao J. Development on thermochemical energy storage based on  
939 CaO-based materials: A review. *Sustain* 2018;10.  
940 <https://doi.org/10.3390/su10082660>.
- 941 [41] Kiplagat JK, Wang RZ, Oliveira RG, Li TX. Lithium chloride - Expanded graphite  
942 composite sorbent for solar powered ice maker. *Sol Energy* 2010;84:1587–94.  
943 <https://doi.org/10.1016/j.solener.2010.06.014>.
- 944 [42] Ishitobi H, Uruma K, Takeuchi M, Ryu J, Kato Y. Dehydration and hydration  
945 behavior of metal-salt-modified materials for chemical heat pumps. *Appl Therm Eng*  
946 2013;50:1639–44. <https://doi.org/10.1016/j.applthermaleng.2011.07.020>.
- 947 [43] British Geological Survey. Lithium Definitions, mineralogy, and deposits. 2016.
- 948 [44] U.S. Geological survey. Lithium. 2017. <https://doi.org/10.3133/pp1802K>.
- 949 [45] National Minerals Information Center U. Mineral Commodity Summaries 2019.  
950 2016.
- 951 [46] Lacabana M. Litio, territorio, ambiente y globalización. *Rev Ciencias Soc*  
952 2018;34:7–15.
- 953 [47] Fornillo B. Geopolítica del Litio Industria, Ciencia y Energía en Argentina. 1st ed.  
954 Buenos Aires: El colectivo, CLACSO; 2015.
- 955 [48] Cot-Gores J, Castell A, Cabeza LF. Thermochemical energy storage and conversion:  
956 A-state-of-the-art review of the experimental research under practical conditions.  
957 *Renew Sustain Energy Rev* 2012;16:5207–24.  
958 <https://doi.org/10.1016/j.rser.2012.04.007>.
- 959 [49] Faraj K, Khaled M, Faraj J, Hachem F, Castelain C. Phase change material thermal  
960 energy storage systems for cooling applications in buildings: A review. *Renew*  
961 *Sustain Energy Rev* 2020;119. <https://doi.org/10.1016/j.rser.2019.109579>.

- 962 [50] Yu N, Wang RZ, Wang LW. Sorption thermal storage for solar energy. *Prog Energy*  
 963 *Combust Sci* 2013;39:489–514. <https://doi.org/10.1016/j.pecs.2013.05.004>.
- 964 [51] Kawasaki H, Watanabe T, Kanzawa A. Proposal of a chemical heat pump with  
 965 paraldehyde depolymerization for cooling system. *Appl Therm Eng* 1999;19:133–  
 966 43.
- 967 [52] N'Tsoukpoe KE, Schmidt T, Rammelberg HU, Watts BA, Ruck WKL. A systematic  
 968 multi-step screening of numerous salt hydrates for low temperature thermochemical  
 969 energy storage. *Appl Energy* 2014;124:1–16.  
 970 <https://doi.org/10.1016/j.apenergy.2014.02.053>.
- 971 [53] N'Tsoukpoe KE, Liu H, Le Pierrès N, Luo L. A review on long-term sorption solar  
 972 energy storage. *Renew Sustain Energy Rev* 2009;13:2385–96.  
 973 <https://doi.org/10.1016/j.rser.2009.05.008>.
- 974 [54] Ö Paksoy H. Thermal Energy Storage for Sustainable Energy Consumption:  
 975 Fundamentals, Case Studies and Design. vol. 234. Turkey: Springer; 2005.
- 976 [55] APPLICATIONS OF THERMAL ENERGY STORAGE IN THE ENERGY  
 977 TRANSITION BENCHMARKS AND DEVELOPMENTS Public Report of IEA  
 978 ECES Annex 30. 2018.
- 979 [56] Pardo P, Deydier A, Anxionnaz-Minvielle Z, Rougé S, Cabassud M, Cognet P. A  
 980 review on high temperature thermochemical heat energy storage. *Renew Sustain*  
 981 *Energy Rev* 2014;32:591–610. <https://doi.org/10.1016/j.rser.2013.12.014>.
- 982 [57] Nakamura N, Miyaoka H, Ichikawa T, Kojima Y. Hydrogen production via  
 983 thermochemical water-splitting by lithium redox reaction. *J Alloys Compd*  
 984 2013;580. <https://doi.org/10.1016/j.jallcom.2013.03.128>.
- 985 [58] Varsano F, Alvani C, La Barbera A, Masi A, Padella F. Lithium manganese oxides



986 as high-temperature thermal energy storage system. *Thermochim Acta* 2016;640:26–  
 987 35. <https://doi.org/10.1016/j.tca.2016.07.018>.

988 [59] Hlongwa NW, Sastre D, Iwuoha E, Carrillo AJ, Ikpo C, Serrano DP, et al. Exploring  
 989 the thermochemical heat storage capacity of  $\text{AMn}_2\text{O}_4$  (A = Li or Cu) spinels. *Solid*  
 990 *State Ionics* 2018;320:316–24. <https://doi.org/10.1016/j.ssi.2018.03.019>.

991 [60] Takasu H, Ryu J, Kato Y. Application of lithium orthosilicate for high-temperature  
 992 thermochemical energy storage. *Appl Energy* 2017;193:74–83.  
 993 <https://doi.org/10.1016/j.apenergy.2017.02.029>.

994 [61] Yan J, Zhao CY. First-principle study of  $\text{CaO}/\text{Ca}(\text{OH})_2$  thermochemical energy  
 995 storage system by Li or Mg cation doping. *Chem Eng Sci* 2014;117:293–300.  
 996 <https://doi.org/10.1016/j.ces.2014.07.007>.

997 [62] Shkatulov AI, Kim ST, Miura H, Kato Y, Aristov YI. Adapting the  $\text{MgO}-\text{CO}_2$   
 998 working pair for thermochemical energy storage by doping with salts. *Energy*  
 999 *Convers Manag* 2019;185:473–81. <https://doi.org/10.1016/j.enconman.2019.01.056>.

1000 [63] Ishitobi H, Hirao N, Ryu J, Kato Y. Evaluation of heat output densities of lithium  
 1001 chloride-modified magnesium hydroxide for thermochemical energy storage. *Ind*  
 1002 *Eng Chem Res* 2013;52:5321–5. <https://doi.org/10.1021/ie302841y>.

1003 [64] Maruyama A, Kurosawa R, Ryu J. Effect of Lithium Compound Addition on the  
 1004 Dehydration and Hydration of Calcium Hydroxide as a Chemical Heat Storage  
 1005 Material. *ACS Omega* 2020. <https://doi.org/10.1021/acsomega.9b04444>.

1006 [65] Shkatulov AI, Aristov Y. Thermochemical Energy Storage using  $\text{LiNO}_3$ -Doped  
 1007  $\text{Mg}(\text{OH})_2$ : A Dehydration Study. *Energy Technol* 2018;6:1844–51.  
 1008 <https://doi.org/10.1002/ente.201800050>.

1009 [66] Shkatulov A, Takasu H, Kato Y, Aristov Y. Thermochemical energy storage by

LiNO<sub>3</sub>-doped Mg(OH)<sub>2</sub>: Rehydration study. *J Energy Storage* 2019;22:302–10.  
<https://doi.org/10.1016/j.est.2019.01.014>.

[67] Takasu H, Kato Y. Reactivity enhancement of lithium orthosilicate for thermochemical energy storage material usage. *Energy Procedia* 2017;131:94–100.  
<https://doi.org/10.1016/j.egypro.2017.09.479>.

[68] Kim ST, Miura H, Takasu H, Kato Y, Shkatulov A, Aristov Y. Adapting the MgO-CO<sub>2</sub> working pair for thermochemical energy storage by doping with salts: Effect of the (LiK)NO<sub>3</sub> content †. *Energies* 2019;12. <https://doi.org/10.3390/en12122262>.

[69] Yu N, Wang RZ, Lu ZS, Wang LW. Study on consolidated composite sorbents impregnated with LiCl for thermal energy storage. *Int J Heat Mass Transf* 2015;58:660–70. <https://doi.org/10.1016/j.ijheatmasstransfer.2015.01.065>.

[70] Yu N, Wang RZ, Wang LW. Theoretical and experimental investigation of a closed sorption thermal storage prototype using LiCl/water. *Energy* 2015;93:1523–34.  
<https://doi.org/10.1016/j.energy.2015.10.001>.

[71] Zhao YJ, Wang RZ, Li TX, Nomura Y. Investigation of a 10 kWh sorption heat storage device for effective utilization of low-grade thermal energy. *Energy* 2016;113:739–47. <https://doi.org/10.1016/j.energy.2016.07.100>.

[72] Li W, Klemesš JJ, Wang Q, Zeng M. Development and characteristics analysis of salt-hydrate based composite sorbent for low-grade thermochemical energy storage. *Renew Energy* 2020;157:920–40. <https://doi.org/10.1016/j.renene.2020.05.062>.

[73] Myagmarjav O, Zamengo M, Ryu J, Kato Y. Energy density enhancement of chemical heat storage material for magnesium oxide/water chemical heat pump. *Appl Therm Eng* 2015;91:377–86.  
<https://doi.org/10.1016/j.applthermaleng.2015.08.008>.

- 1034 [74] Zhang YN, Wang RZ, Li TX. Thermochemical characterizations of high-stable  
 1035 activated alumina/LiCl composites with multistage sorption process for thermal  
 1036 storage. *Energy* 2018;156:240–9. <https://doi.org/10.1016/j.energy.2018.05.047>.
- 1037 [75] Zhang Y, Wang R, Li T, Zhao Y. Thermochemical characterizations of novel  
 1038 vermiculite-LiCl composite sorbents for low-temperature heat storage. *Energies*  
 1039 2016;9. <https://doi.org/10.3390/en9100854>.
- 1040 [76] Liu H, Nagano K, Togawa J. A composite material made of mesoporous siliceous  
 1041 shale impregnated with lithium chloride for an open sorption thermal energy storage  
 1042 system. *Sol Energy* 2015;111:186–200.  
 1043 <https://doi.org/10.1016/j.solener.2014.10.044>.
- 1044 [77] Tokarev MM, Gordeeva LG, Shkatulov AI, Aristov YI. Testing the lab-scale “Heat  
 1045 from Cold” prototype with the “LiCl/silica – methanol” working pair. *Energy*  
 1046 *Convers Manag* 2018;159:213–20. <https://doi.org/10.1016/j.enconman.2017.12.099>.
- 1047 [78] Casey SP, Elvins J, Riffat S, Robinson A. Salt impregnated desiccant matrices for  
 1048 “open” thermochemical energy storage - Selection, synthesis and characterisation of  
 1049 candidate materials. *Energy Build* 2014;84:412–25.  
 1050 <https://doi.org/10.1016/j.enbuild.2014.08.028>.
- 1051 [79] Sutton RJ, Jewell E, Elvins J, Searle JR, Jones P. Characterising the discharge cycle  
 1052 of CaCl<sub>2</sub> and LiNO<sub>3</sub> hydrated salts within a vermiculite composite scaffold for  
 1053 thermochemical storage. *Energy Build* 2018;162:109–20.  
 1054 <https://doi.org/10.1016/j.enbuild.2017.11.068>.
- 1055 [80] Sutton R, Jewell E, Searle J, Elvins J. Discharge performance of blended salt in  
 1056 matrix materials for low enthalpy thermochemical storage. *Appl Therm Eng*  
 1057 2018;145:483–93. <https://doi.org/10.1016/j.applthermaleng.2018.09.052>.

- 1058 [81] Jabbari-Hichri A, Bennici S, Auroux A. Enhancing the heat storage density of silica–  
1059 alumina by addition of hygroscopic salts (CaCl<sub>2</sub>, Ba(OH)<sub>2</sub>, and LiNO<sub>3</sub>). *Sol Energy*  
1060 *Mater Sol Cells* 2015;140:351–60. <https://doi.org/10.1016/j.solmat.2015.04.032>.
- 1061 [82] Li S, Huang H, Yang X, Bai Y, Li J, Kobayashi N, et al. Hydrophilic substance  
1062 assisted low temperature LiOH·H<sub>2</sub>O based composite thermochemical materials for  
1063 thermal energy storage. *Appl Therm Eng* 2018;128:706–11.  
1064 <https://doi.org/10.1016/j.applthermaleng.2017.09.050>.
- 1065 [83] Kim ST, Kurahashi C, Hoshino H, Takahashi C, Tamura Y, Takasu H, et al. Thermal  
1066 driving demonstration of Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub>/zeolite thermochemical energy storage  
1067 system for efficient high-temperature heat utilizations. *ISIJ Int* 2019;59:721–6.  
1068 <https://doi.org/10.2355/isijinternational.ISIJINT-2018-428>.
- 1069 [84] Takasu H, Hoshino H, Tamura Y, Kato Y. Performance evaluation of  
1070 thermochemical energy storage system based on lithium orthosilicate and zeolite.  
1071 *Appl Energy* 2019;240:1–5. <https://doi.org/10.1016/j.apenergy.2019.02.054>.
- 1072 [85] Kim ST, Nihei T, Kurahashi C, Hoshino H, Takasu H, Kato Y. Kinetic study of  
1073 lithium orthosilicate pellets for high-temperature chemical heat pumps. *Energy*  
1074 *Storage* 2019;1. <https://doi.org/10.1002/est2.72>.
- 1075 [86] Yang X, Huang H, Wang Z, Kubota M, He Z, Kobayashi N. Facile synthesis of  
1076 graphene oxide-modified lithium hydroxide for lowerature chemical heat storage.  
1077 *Chem Phys Lett* 2016;644:31–4. <https://doi.org/10.1016/j.cplett.2015.11.033>.
- 1078 [87] Grekova A, Gordeeva L, Aristov Y. Composite sorbents “li/Ca halogenides inside  
1079 Multi-wall Carbon Nano-tubes” for Thermal Energy Storage. *Sol Energy Mater Sol*  
1080 *Cells* 2016;155:176–83. <https://doi.org/10.1016/j.solmat.2016.06.006>.
- 1081 [88] Yang X, Li S, Huang H, Li J, Kobayashi N, Kubota M. Effect of carbon

1082 nanoadditives on lithium hydroxide monohydrate-based composite materials for low  
 1083 temperature chemical heat storage. *Energies* 2017;10.  
 1084 <https://doi.org/10.3390/en10050644>.

1085 [89] Grekova AD, Gordeeva LG, Lu Z, Wang R, Aristov YI. Composite “LiCl/MWCNT”  
 1086 as advanced water sorbent for thermal energy storage: Sorption dynamics. *Sol*  
 1087 *Energy Mater Sol Cells* 2018;176:273–9.  
 1088 <https://doi.org/10.1016/j.solmat.2017.12.011>.

1089 [90] Li S, Huang H, Li J, Kobayashi N, Osaka Y, He Z, et al. The effect of 3D carbon  
 1090 nanoadditives on lithium hydroxide monohydrate based composite materials for  
 1091 highly efficient low temperature thermochemical heat storage. *RSC Adv*  
 1092 2018;8:8199–208. <https://doi.org/10.1039/c8ra00269j>.

1093 [91] Sérgio Maravilhas-Lopes (IES-ICS Federal University of Bahia B. Sustainable  
 1094 Innovation Projects From Patent Information to Leverage Economic Development.  
 1095 In *Handbook of Research on Emerging Technologies for Effective Project*  
 1096 *Management*. IGI Global; 2020. <https://doi.org/10.4018/978-1-5225-9993-7.ch010>.

1097 [92] Mariani MS, Medo M, Lafond F. Early identification of important patents: Design  
 1098 and validation of citation network metrics. *Technol Forecast Soc Change*  
 1099 2019;146:644–54. <https://doi.org/10.1016/j.techfore.2018.01.036>.

1100 [93] Yuanliang M. Thermal storage and energy accumulation conversion device Patent.  
 1101 B101876460, 2012.

1102 [94] Cai Jingfu LG, Xucan S, Congyi S, Yaofang H, Gaofeng K, Liangyi W. A soil-  
 1103 source cold-storage heat accumulation system device that is used for hot peak  
 1104 regulation usefulness of steam power plant. U205641673, 2016.

1105 [95] Haonan Z. Sludge and garbage carbonizing system. A107400525, 2017.

- 1106 [96] Wu Dianying LZ, Hua W. Cold and hot antithetical couplet of fused salt energy  
1107 storage supplies device. U207196936, 2018.
- 1108 [97] Han Yongwei DH, Xiang L. Cooling heating and power triple co-generation peak  
1109 shaving system. U207196936, 2018.
- 1110 [98] Tong Hang XH, Liang S, Baoyu W. Energy supply system synthesizes in hospital  
1111 based on gas turbine. U207333026, 2018.
- 1112 [99] Hu Hemin ZM, Shiqiang L, Yuyan J, Yongxian G. Device giving consideration to  
1113 safe aestivation and electric power peak-load regulation of thermal power air cooled  
1114 condenser. A108678820, 2018.
- 1115 [100] Deng Yanan ZR, Yongfeng H, Jianbiao L, Aiping Z. System for utilize internal -  
1116 combustion engine cylinder liner water cooling internal -combustion engine to admit  
1117 air. U208534652, 2019.
- 1118 [101] Chuanfeng G. The fuel gas distributed energy station can stabilize heat and cold  
1119 supply balance structure of gas turbine load. U209053697, 2019.
- 1120 [102] Tao S. Malt waste heat utilization system of cooking with heat-retaining function.  
1121 U207214448, 2018.
- 1122 [103] Yin Wenjun CJ, Ailan T, Gang L. Solar heating and refrigerating system.  
1123 A105674624, 2016.
- 1124 [104] Tan Junyi JW, Yuanchuan Z. Intelligent solar air-conditioning system. A106032918,  
1125 2016.
- 1126 [105] Guan Jingdong LD, Jianhui H, Liangcheng O. Solar energy power generation light  
1127 field system. U207195109, 2018.
- 1128 [106] Zhao Shanguo ZX, Bo S. Solar double-effect absorption heat pump drying system  
1129 with thermal storage function. B107036402, 2019.

1130 [107] Chen Jianhao TJ, Jianbo B, Tianma G, Guangqing W, Guofang Z, Fei C, et al.  
 1131 Combined solar LiBr absorption air conditioning system. B107388620, 2020.  
 1132 [108] Jiang Shaohui WC, Bin L, Bin L. Solar thermal energy steam type refrigerating  
 1133 system. U208365864, 2019.  
 1134 [109] Jiang Shaohui WC, Bin L, Bin L. Solar water -heating type refrigerating system.  
 1135 U208365865, 2019.  
 1136 [110] Tongqiang L. Solar energy and engine exhaust heat dual-power refrigeration air  
 1137 conditioner for vehicle. B101504224, 2012.  
 1138 [111] Rong Z. Solar energy and geothermal energy composite energy supply system for  
 1139 rural residence buildings in Huna Province. A108386933, 2018.  
 1140 [112] Bai J, Chen J, Huai X, Wang G, Xia X, Liu Y, et al. Combined energy-based solar  
 1141 LiBr absorption trigeneration system. WO/2019/056604, 2019.  
 1142 [113] Ma Hongting LZ, Junwen L, Chen L, Fan Y. Cooling and heating system provide  
 1143 multiple forms of energy to complement each other. U208349622, 2019.  
 1144 [114] Zhongbo Y. Waste heat recovery type off-peak electricity energy storage heating  
 1145 system. U209246210, 2019.  
 1146 [115] Xiong Xingcai LX. Device and method for performing distributed energy utilization  
 1147 on molten salt stored energy. B107289664, 2020.  
 1148 [116] Wei Qi LM. Heat energy storage method based on metal hydride and metal organic  
 1149 framework material. A107941062, 2018.  
 1150 [117] Wei Qi LM. Heat energy storage method based on metal hydride and covalent  
 1151 organic framework material. A107941063, 2018.  
 1152