

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

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### ARTICLE INFO

#### Keywords:

Lithium compounds  
Thermochemical storage (TCS)  
Patents  
Technological and cost challenges  
Energy storage density  
TCS operational Conditions

### ABSTRACT

The world is currently going through significant changes in technology, and alongside these advances, new developments of strategies to store and supply energy are crucial for the widespread use of consumer electronics and white goods. Besides, the impacts of greenhouse gas emissions and climate change are exerting pressure towards less polluting sources of energy and strategies to diminish energy losses. In this environmental context, lithium compounds are an attractive alternative to store energy in thermal energy storage systems due to their thermodynamic features, which make such compounds a relevant strategy for energy storage, for instance, capturing residual energy from several industrial activities. Here a review of the current state of the art and new technological advances reflected by the scientific literature and the patented inventions using lithium as a relevant compound for thermochemical energy storage has been performed. Throughout a search on different databases, it is proposed a simplified process to support our findings and the analysis of this data. Thus, several important advances in thermochemical energy storage using chemical reaction and sorption systems were evidenced. The literature also showed that the majority of the analysed investigation included in our data set are based on sorption technologies. This review suggests the need for systematisation in reporting critical data to facilitate a common understanding with regards to the advances in energy storage, especially when referring to heat storage density. The importance of lithium in thermochemical systems in the future will probably keep increasing, particularly in systems where several lithium salts have shown to be excellent doping agents and working pairs of materials included in different matrices.

## 1. Introduction

### 1.1. Lithium as a milestone for energy storage

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) [3,4] and batteries coupled to power plants [5]. As a consequence, the demand for this mineral has intensified in recent years, leading to an increase in industrial production. As a result, during the period 2009–2019, the world mining production of lithium increased from 18,000 to 77,000 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 tonnes in 2019, respectively [6,7]. As the demand of lithium compounds has grown, so the technologies for the extraction of lithium and the production of its compounds have improved throughout the world, as well as the recycling of spent Li batteries for metal recovery [4]. This enhanced accessibility of lithium compounds means, it is vitally

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important to analyse the potential that these materials have in different areas, including thermal energy storage.

### 1.2. Lithium for thermal energy storage

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

TES materials, including lithium compounds [8], play a strategic role in TES systems for industrial waste heat recovery [9–11], concentrated solar power (CSP) plants [12–14], and buildings [15–17] amongst other applications, due to their large heat storage capacity [18]. 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 [19]. 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 [20], as the reactants (energy storing materials) can be stored at ambient temperature.

Due to the high-energy density of TCS systems, anticipated applications of such technologies include storage in CSP plants, in residential and commercial buildings, as well as their use for heating or cooling buildings [21]. 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 [22], SrBr<sub>2</sub> [23], MgSO<sub>4</sub> [24], and CaO [25]. The potential of such chemical reactions places thermochemical energy storage as one of the most advantageous techniques for storage in CSP plants [26]. 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 [27] which conducted an evaluation of types of energy storage, including TCS systems and applications. However, there are more specific reviews made according to the type of application, such as CSP plants [26,28–31], high-temperature TCS systems [32–34], power grid support [35], building applications [36] and evaluation of thermochemical material for their implementation in TCS systems [37–41].

### 1.3. Problem statement

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 thermochemical material, with the potential to improve the storage density of a system [8]. This has been demonstrated by Kiplagat et al. [42] and Ishitobi et al. [43]. Kiplagat et al. 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 pure Mg(OH)<sub>2</sub> and LiCl-modified Mg(OH)<sub>2</sub> as a potential new material for chemical heat pumps – a 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. Moreover, the application of Li compounds for thermochemical energy storage remains in an emerging phase and it is scarcely documented;

information on new Li thermochemical materials is still dispersed.

Considering the early stage of development of this technology mentioned above and the growing applications of lithium compounds, 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

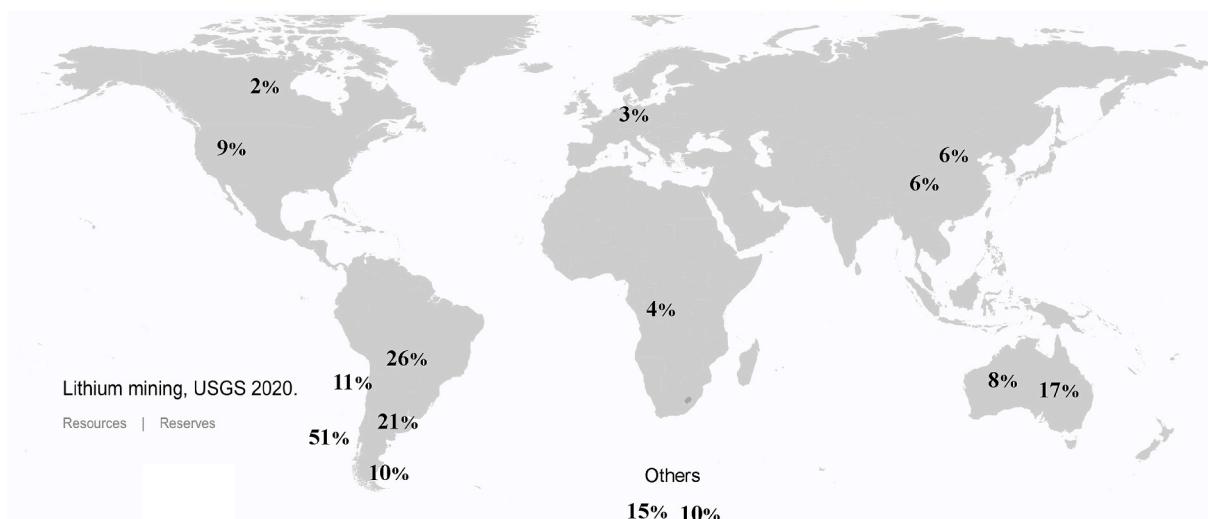
One relevant criterion to assess the applicability of specific materials is the abundance and availability of the resource. The abundance of material will broadly impact the potential for exploitation and the capacity to maintain a relatively secure stock. The availability refers to the accessibility of a resource. In this respect, lithium abundance and production levels are continually monitored by several governmental agencies and treated as a key commodity [7].

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 [44]. 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%) [45].

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 [46]. 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 5323 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 [7].

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% (Fig. 1) [7]. 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 [47]. Although there are countries with abundant resources, it is not necessarily economically feasible to exploit them because of poor accessibility and levels of impurities such as magnesium and iron [45].

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



**Fig. 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). Based on information from Ref. [7].

important (Fig. 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 [7].

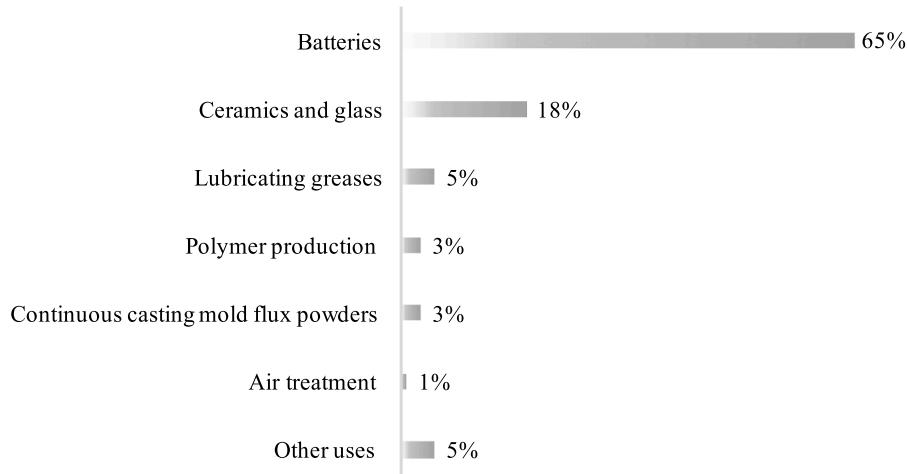
The use of lithium in rechargeable batteries for the automotive industry constitutes a potential benefit for the world population and the environment since they would make it possible for vehicles to use energy from renewable carbon-free sources (e.g. solar, hydroelectric or wind power) instead of traditional fuel sources (e.g. naphtha, diesel) reducing emissions of carbon dioxide, a pollutant considered to be one of the main causes of global warming [48].

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

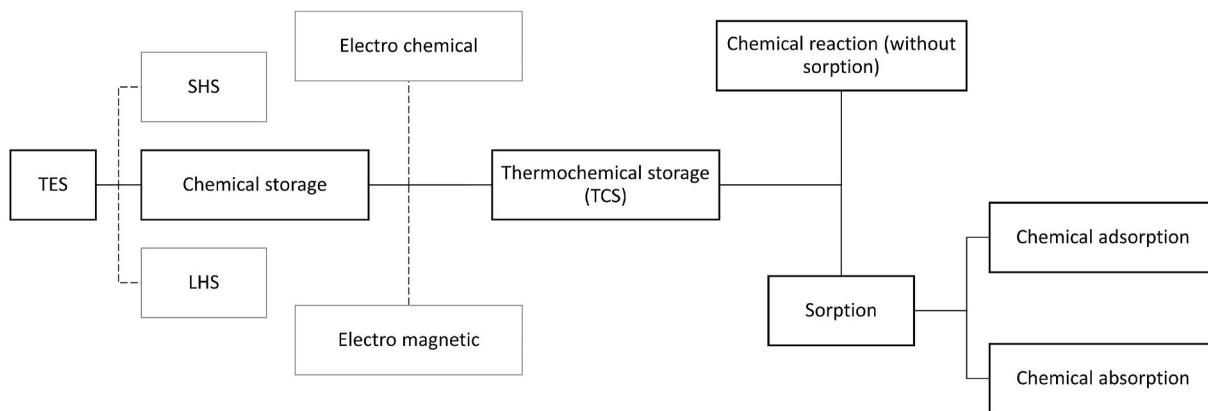
TCS systems are a form of chemical storage, and a part of a much wider group of TES technologies, which also includes SHS and LHS

(Fig. 3). In the literature it is possible to find multiple schemes of classification of TCS systems [49,50]. As shown in Fig. 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; absorption refers to the molecular assimilation within the bulk of a solid or liquid, and adsorption to the accumulation of molecules on the surface of a solid or liquid. The present classification was proposed by Yu et al. [51], a 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.

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 [52]. All reversible physicochemical reactions within TCS systems can be described by Eq. (1), in which A is a reactant



**Fig. 2.** Lithium end applications, 2019. Based on [7].



**Fig. 3.** Scheme of TES classification, based on [51].

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 a result of this reaction [53].



This classical TCS system is divided into three main processes, as shown in Fig. 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.

As previously explained, TCS can be classified into chemical reactions and sorption processes (Fig. 3) [51]. 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 [54]. The adsorption and desorption process on solid materials is schematically shown in Fig. 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 material, driving out the adsorbed component

(e.g. water molecules in Fig. 5) from the inner surface. In the reverse reaction (i.e. desorption), 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.

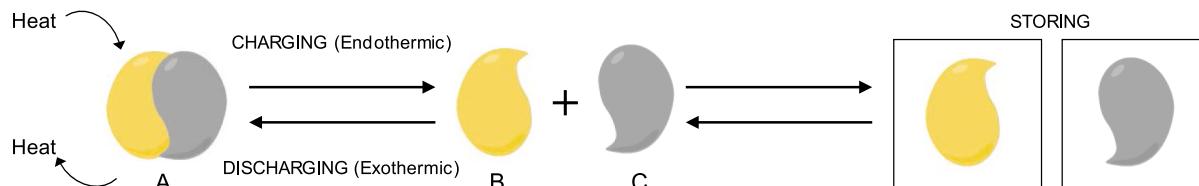
The main advantages of thermochemical storage systems are their high storage density ( $0.5\text{--}3 \text{ GJ/m}^3$ ) and negligible heat losses over long periods [20]. Evidence of this potential is the existence of hybrid cars that run on electrical energy and thermochemical energy, a project that is currently in the pilot phase of development [56]. However, TCS systems are not without their disadvantages; the main drawbacks of such thermochemical storage technologies are 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 [57]. 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. Methodologies applied to lithium compounds for TCS

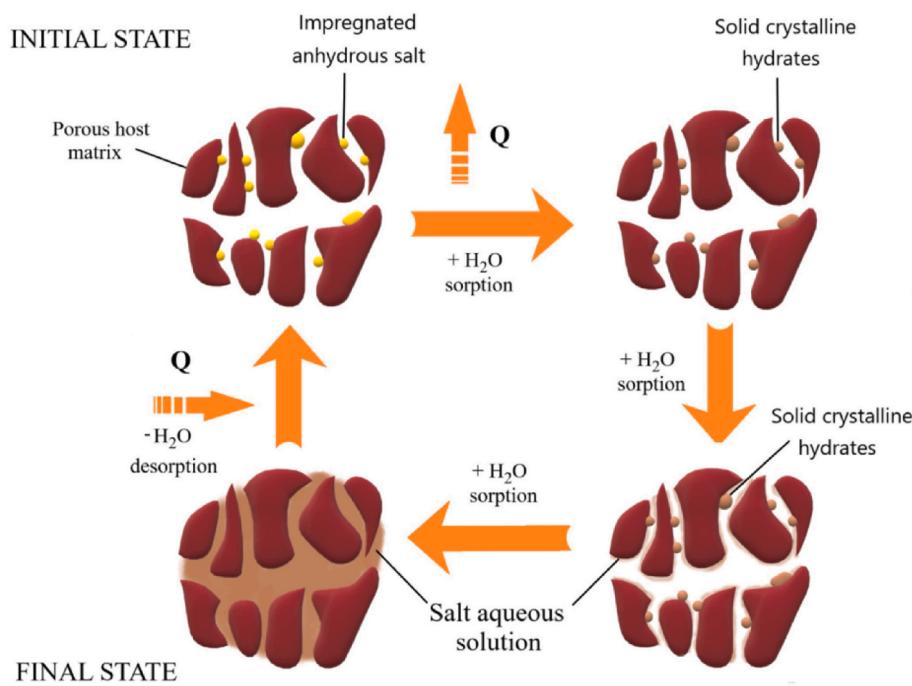
The analysis of TCS system literature categorised research according to the classifications proposed in Fig. 3: those investigations using chemical reaction (without sorption) and those with sorption as the basis. The fact that these two classifications involve similar mechanisms in many cases makes it difficult to distinguish clear differences and to sort out the literature based on clearly defined criteria [51]. However, an effort was made to classify the literature obtained from the search process detailed in SI Figure S1. 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 based on chemical reactions

Within the *chemical reaction* classification of TCS, it was possible to make two clear distinctions; lithium as a working pair and lithium as a



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



**Fig. 5.** Adsorption and desorption process of water on a porous matrix. Based on [55].

doping agent. **Table 1** presents the use of lithium salts as the main functional compound or working pair, and **Table 2** shows studies using lithium compounds as a doping agent.

#### 4.1.1. Lithium compounds as a working pair

The main lithium compounds included in **Table 1** were LiOH [58], LiMnO<sub>2</sub> [59,60], and Li<sub>4</sub>SiO<sub>4</sub> [61], which were tested as part of different working pairs reactions, for instance, using O<sub>2</sub> and CO<sub>2</sub> showing varied results [59,61]. 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. [58] 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 [59] and

Hlongwa [60] 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 and 1000 °C, with no deterioration detected when multiple redox cycles were performed (**Fig. 6**), concluding that adding lithium to the conventional manganese oxide thermochemical cycle is highly favourable. Similarly, Takasu et al. [61] proposed the use of lithium orthosilicate/carbon dioxide (Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub>) reaction system for applications in TCS and chemical heat pumps (CHP) at approximately 700 °C. In this TCS system, decarbonation and carbonation –a reversible chemical process of endothermic decomposition in which CO<sub>2</sub> is released from the reactant and then recaptured through the equivalent exothermic reaction– were used for heat storage, and for heat output respectively. The role of the process of decarbonation/carbonation is based on the cyclic emission and storage of energy by the reactants in the chemical reaction –when CO<sub>2</sub> is released during the decomposition stage, energy is chemically stored, and when CO<sub>2</sub> is supplied back to the reaction energy is produced. The results showed that Li<sub>4</sub>SiO<sub>4</sub> has a cyclic stability at 400 to 900 °C with no deterioration over 5 cycles and that the carbonation and decarbonation performance of Li<sub>4</sub>SiO<sub>4</sub> were sufficient for use as TCS material at around 700 °C (**Fig. 7**). Furthermore, the results indicate that by regulating the CO<sub>2</sub> pressure, the temperature for heat storage and heat output could be

**Table 1**

Lithium compounds used as a working pair.

Lithium compound	Working pair	Reactions	ΔH [kJ/mol]	T [°C]	q <sub>v</sub> [kJ/L]	q <sub>g</sub> [kJ/kg]	References
LiOH	LiOH/Li	2LiOH(s) + 2Li(l) → 2Li <sub>2</sub> O(s) + H <sub>2</sub> (g)	-232	500	n.a	n.a	[58]
		2Li <sub>2</sub> O(s) → Li <sub>2</sub> O <sub>2</sub> (s) + 2Li(g)	883	800	n.a	n.a	
		Li <sub>2</sub> O <sub>2</sub> (s) + H <sub>2</sub> O(l) → 2LiOH(s) + 1/2O <sub>2</sub> (g)	-51	300	n.a	n.a	
LiMnO <sub>2</sub>	LiMnO <sub>2</sub> /O <sub>2</sub>	3LiMnO <sub>2</sub> (s) + 1/2O <sub>2</sub> (g) ↔ Li <sub>2</sub> MnO <sub>3</sub> (s) + LiMn <sub>2</sub> O <sub>4</sub> (s)	21(ox); 25(red)	800–1000	n.a	n.a	[59]
LiMnO <sub>2</sub>	LiMnO <sub>2</sub> /O <sub>2</sub>	3LiMnO <sub>2</sub> (s) + 1/2O <sub>2</sub> (g) ↔ Li <sub>2</sub> MnO <sub>3</sub> (s) + LiMn <sub>2</sub> O <sub>4</sub> (s)	37	700	n.a	n.a	[60]
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) ↔ Li <sub>2</sub> CO <sub>3</sub> (s) + Li <sub>2</sub> SiO <sub>3</sub> (s)	-94	650–700	750 †	780 †	[61]
				650–700	650 ‡	670 ‡	

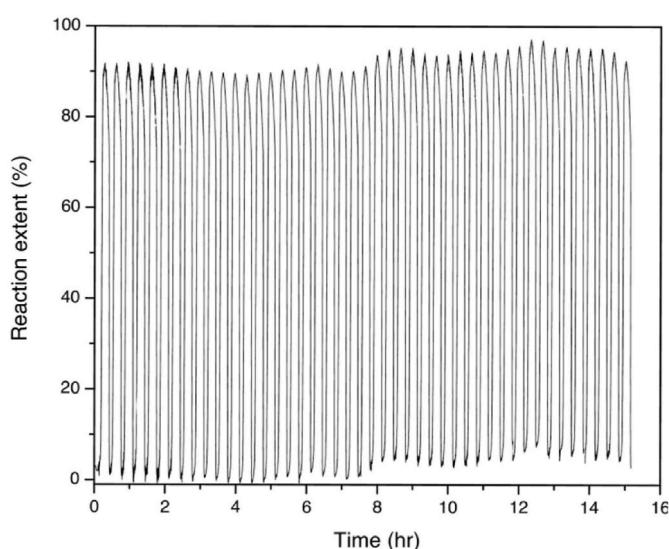
Note: ΔH –Heat of reaction; T –temperature of reaction; q<sub>v</sub> –volumetric thermal energy density; q<sub>g</sub> –gravimetric thermal energy density; n.a. –not available. †Used in TCS, ‡used in chemical heat pump (CHP).

**Table 2**

Lithium compounds used as a 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) ⇌ 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	[64]
LiOH·H <sub>2</sub> O	CaO/H <sub>2</sub> O	CaO(s) + H <sub>2</sub> O(g) ⇌ Ca(OH) <sub>2</sub> (s)	109.3	430 (dehydration)	n.a	n.a	n.a	n.a	0.11	[62]
LiOHCe (NO <sub>3</sub> ) <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) ⇌ MgO(s) + H <sub>2</sub> O(g)	90.0	270	891.0–916.0	n.a	n.a	2.3 (H <sub>2</sub> O)	n.a	[66]
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) ⇌ 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	[70]
LiNO <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) ⇌ 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	[67]
LiNO <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) ⇌ 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	[68]
LiNO <sub>3</sub>	MgO/H <sub>2</sub> O	Mg(OH) <sub>2</sub> (s) ⇌ MgO(s) + H <sub>2</sub> O(g)	431.5–173.9	250–400	1220	n.a	n.a	n.a	n.a	[69]
LiKNO <sub>3</sub> CH <sub>3</sub> COOLi	MgO/CO <sub>2</sub>	MgCO <sub>3</sub> (s) ⇌ 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	[63]
LiKNO <sub>3</sub>	MgO/CO <sub>2</sub>	MgO(s) + CO <sub>2</sub> (g) ⇌ MgCO <sub>3</sub> (s)	-116.4	~400 (carbonation); 300–350 (decarbonation)	1180–1250	n.a	n.a	50–101 (CO <sub>2</sub> )	n.a	[71]
LiCl LiOH Li <sub>2</sub> CO <sub>3</sub>	CaO/H <sub>2</sub> O	CaO(s) + H <sub>2</sub> O(g) ⇌ Ca(OH) <sub>2</sub> (s)	-104.4	350 (dehydration); 110 (hydration)	450–670	n.a	n.a	7.4 (H <sub>2</sub> O)	n.a	[65]

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.



**Fig. 6.** Cyclical oxidation/reduction of LiMnO<sub>2</sub> in the 800–1000 °C temperature range [59].

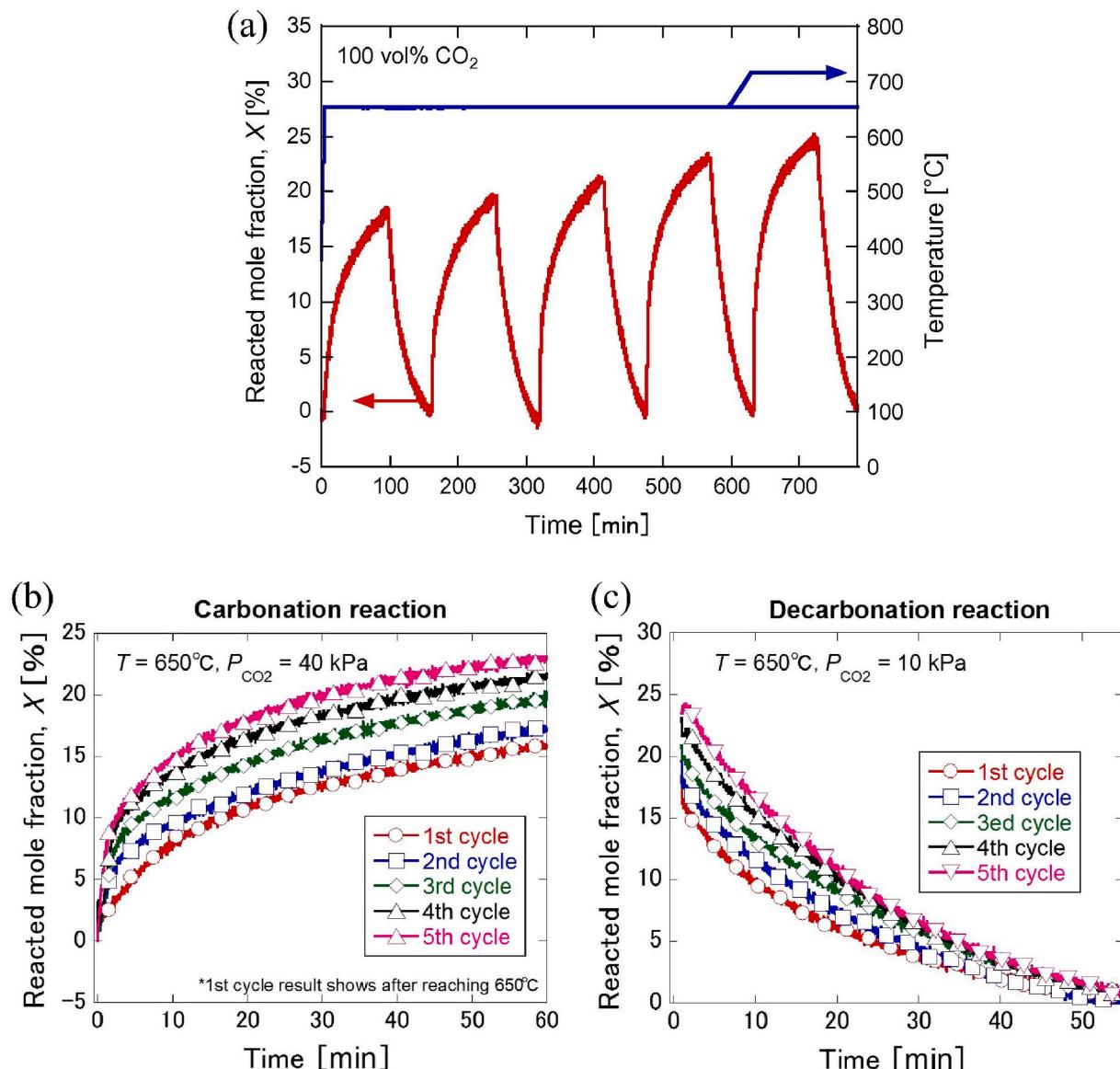
controlled.

#### 4.1.2. Lithium compounds as a doping agent

Lithium has not only been used as the main reactant component (i.e. working pair). In fact, there are a number of investigations in which lithium compounds can be also applied as an adjuvant or enhancer in the process of thermal storage, this has been frequently referred under the concept of *doping*. The doping effect of lithium helps to promote the

thermal storage capacity of other working pairs (e.g. MgO and CaO) by changing the reaction kinetics. This effect includes the reduction of the dehydration barrier, decreasing the reaction temperature at which chemical bonds dissociate, for instance promoting the hydroxyl (OH<sup>-</sup>) bond-braking from calcium hydroxide (Ca(OH)<sub>2</sub>) [62]. Additionally, lithium doping has been shown to promote the process of carbonation, an effect presented by Shkatulov et al. [63] where applying 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 the carbonation conversion, enhancing the process of heat storage.

The lithium salts used as dopants are listed in Table 2. As it can be seen in this table, the main doping lithium-based salts are LiCl [64,65], LiOH [62,65,66], LiNO<sub>3</sub> [67–69], Li<sub>4</sub>SiO<sub>4</sub> [70] and LiKNO<sub>3</sub> [63,71]. These salts have been used in multiple investigations, showing good thermal stability and expanding the applicability of the compounds as heat storage materials. Several studies have been conducted in order to investigate the effect that addition of lithium compounds as doping agents has on the dehydration and hydration reactions of different compounds. For instance, Yan and Zhao [62] investigated the process of dehydration utilising 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. [64], 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



**Fig. 7.** Durability of  $\text{Li}_4\text{SiO}_4$  reactivity observed at  $700^\circ\text{C}$ . (b) Comparison of carbonation ( $P_{\text{CO}_2} = 80 \text{ kPa}$ ;  $t = 30 \text{ min}$ ) and (c) decarbonation reaction ( $P_{\text{CO}_2} = 10 \text{ kPa}$ ;  $t = 90 \text{ min}$ ) [61].

and a 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  $\text{LiCl}/\text{MgO}$  system can be used as a new material alternative for applications in TCS. Likewise, Shkatulov et al. [67], performed a dehydration study using magnesium hydroxide doped with lithium nitrate ( $\text{LiNO}_3/\text{Mg}(\text{OH})_2\cdot\text{Y}$  (where Y is the  $\text{LiNO}_3$  content)). The results indicate that lithium salt diminished the dehydration start temperature by  $76^\circ\text{C}$  in the final material; while the reaction heat remained almost unaffected below 5 wt% of lithium salt content. The  $\text{LiNO}_3$ -doped  $\text{Mg}(\text{OH})_2$  was able to store up to 800–1000 kJ/kg at a temperature below  $235^\circ\text{C}$  (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 (Fig. 8). Moreover, when 10 wt%  $\text{LiNO}_3$  was added to  $\text{Mg}(\text{OH})_2$ , the reaction rate constant k was higher ( $\sim 10^{-2} \text{ s}^{-1}$ ), which has a sluggish dehydration process [69].

Similarly, lithium compounds have also been used to study the effect of doping in carbonation/decarbonation reactions. Skatulov et al. [63] 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 (Fig. 9). In the same way, Kim et al. [71] 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  $290$ – $350^\circ\text{C}$  (Fig. 10). Overall and as illustrated throughout this section, several lithium salts are promising compounds to enhance the functionality and range of application of heat storage systems.

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 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

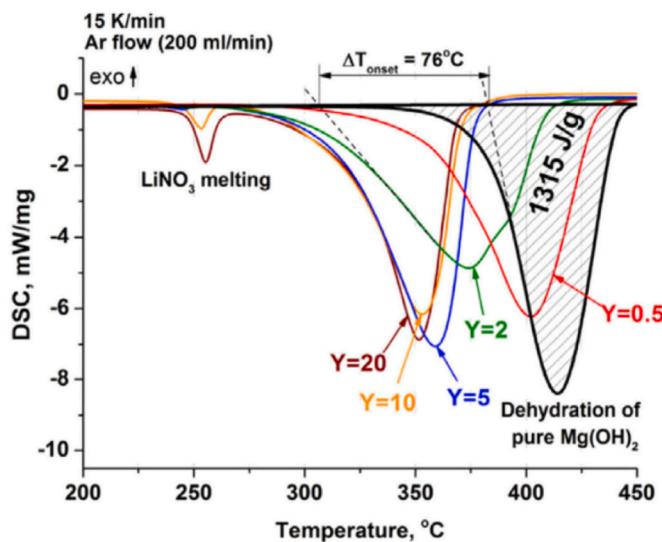


Fig. 8. DSC-curves and the dehydration temperature of  $\text{LiNO}_3/\text{Mg}(\text{OH})_2$ . Y [67].

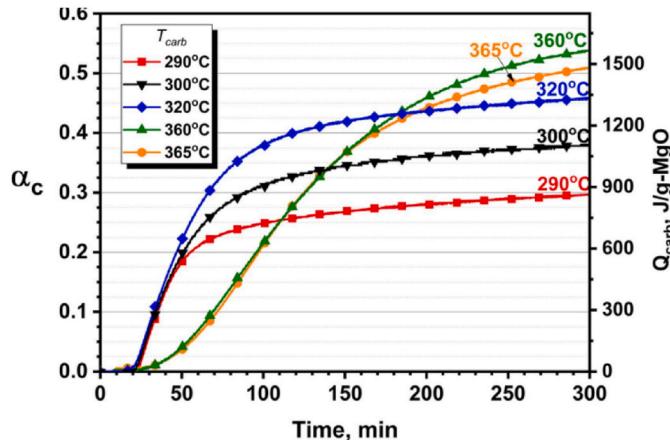


Fig. 9. Carbonation kinetics of  $(\text{LiK})\text{NO}_3/\text{MgO}$  [63].

agents to modify the reaction conditions of other pure salts in i)

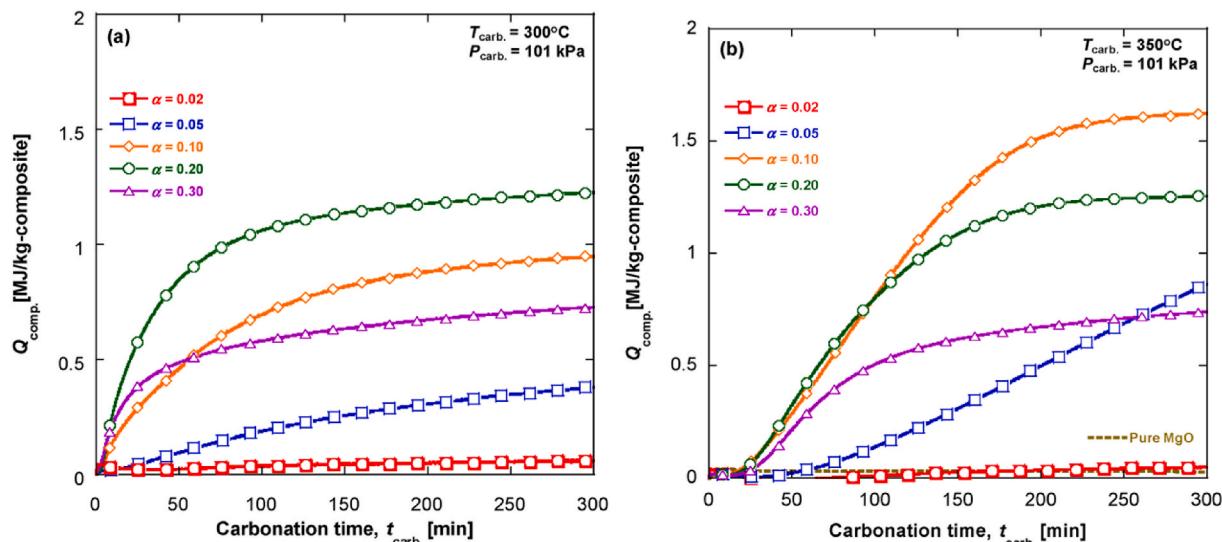


Fig. 10. Specific useful heat,  $Q_{\text{comp}}$ , as a function of the carbonation time at (a)  $300^\circ\text{C}$  and (b)  $350^\circ\text{C}$  [71].

dehydration and hydration reactions to reduce both the energy barrier and temperature of the reaction, maintaining 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 –14 research documents in total–, making it challenging to determine a specific trend in the usage of working pairs or doping based on lithium salts.

#### 4.2. Lithium in TCS based on 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 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 the 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 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) [72,73], expanded graphite (EG) [74–78], activated alumina (AA) [79], expanded vermiculite (EVM) [80], Wakkai shale (WSS) [81], silica gel (SG) [82,83], vermiculite (VM) [84–86], silica-alumina (S-AA) [87], zeolite (13X-Z, NaY-Z, Z) [88–91], graphene oxide (GO) [92]. The following sections will provide more details about the application of commonly found matrices in the related literature.

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

Working par													
Lithium compound/Sorbate	Porous matrix	Li content [%]	Sorbate uptake [g/g]	T [°C]	p [kPa]	λ [W/m K]	K <sub>p</sub> × 10 <sup>-12</sup> [m <sup>2</sup> ]	q [kW]	ε	Recovered heat [kJ]	ESD [kJ/kg]/[MJ/m <sup>3</sup> ]	Efficiency [%]	Ref.
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	[72]
LiCl/H <sub>2</sub> O	AC mixed with ENG-TSA and SS	40	0.52	85 <sup>c</sup> ; 40 <sup>d</sup>	n.a	2.6	3.43	0.86	0.7	2517	874 (consolidated sorbent)/–; 2622 (LiCl)/–	93	[73]
LiCl/H <sub>2</sub> O	EG	n.a	n.a	85 <sup>c</sup> ; 40 <sup>d</sup>	0.87–1.68	2.25	4.65	6.50	0.705	n.a	3142/–	94	[74]
LiCl/H <sub>2</sub> O	AA	14.68	0.41	120 <sup>c</sup>	n.a	0.37	n.a	n.a	0.29	n.a	1041.5/–	n.a	[79]
LiCl/H <sub>2</sub> O	EVM	32.60	1.41	<100	n.a	n.a	n.a	n.a	n.a	n.a	4356/6178	n.a	[80]
LiCl/H <sub>2</sub> O	MWCNTs	41–42	0.09; 0.16; 0.26; 0.35; 0.52	75 <sup>c</sup> ; 35 <sup>d</sup>	0.88 (ad); 1.72 (des)	n.a	n.a	11.2 <sup>+</sup>	n.a	n.a	1700/–	n.a	[95]
LiCl/H <sub>2</sub> O	WSS	9.6	0.6 <sup>ad</sup> ; 0.1 <sup>des</sup>	25–150	2.218	n.a	n.a	n.a	55	539.4 (10 h); 327.1 (4 h)	–/180	65.7 (10 h); 39.8 (4 h)	[81]
LiCl/H <sub>2</sub> O	MWCNTs	44	1.04	75 <sup>c</sup> ; 35 <sup>d</sup>	0.9; 1.7; 3.2; 5.6	n.a	n.a	n.a	n.a	n.a	1700 <sup>ST</sup> /–	n.a	[93]
LiCl/CH <sub>3</sub> OH	MWCNTs	44	1.65	75 <sup>c</sup> ; 35 <sup>d</sup>	7.3; 9.6; 12.7; 16.5; 21.3; 27.3	n.a	n.a	n.a	n.a	n.a	1600 <sup>LT</sup> /–	n.a	
LiCl/CH <sub>3</sub> OH	SG	20	0.4 <sup>c</sup>	34–53	n.a	n.a	n.a	6.0–10.8 <sup>+</sup>	n.a	n.a	620/–	n.a	[82]
LiCl/NH <sub>3</sub> /H <sub>2</sub> O	EG/AC	30	n.a	22 <sup>c</sup> ; 67 <sup>d</sup>	30	76.46	n.a	n.a	0.72	n.a	–/–	n.a	[77]
LiBr/H <sub>2</sub> O	EG	10	n.a	300 <sup>c</sup> ; 110 <sup>d</sup>	57.8	1.91	n.a	n.a	n.a	n.a	–/815.4	n.a	[76]
LiNO <sub>3</sub> /H <sub>2</sub> O	VM	24	n.a	<130 <sup>c</sup>	n.a	0.0659	n.a	n.a	n.a	n.a	286.9/–	n.a	[84]
LiBr*/H <sub>2</sub> O	VM	24	n.a	<130 <sup>c</sup>	n.a	0.0691	n.a	n.a	n.a	n.a	268.9/–	n.a	
LiBr/H <sub>2</sub> O	SG*	37	0.4 (low scale)	30 <sup>ad</sup> ; 80, 120 <sup>des</sup>	1.25	n.a	n.a	n.a	n.a	n.a	–/428.4 (80 °C, low scale) <sup>†</sup>	n.a	[83]
			53*	0.6 (low scale); 0.22–0.25 (high scale)	30 <sup>ad</sup> ; 80, 120 <sup>des</sup>	1.25	n.a	0.286 <sup>+</sup> (high scale)	n.a	n.a	–/939.6 (80 °C, low scale)) <sup>†</sup> ; –/1371.6 (120 °C, low scale) <sup>†</sup> ; –/576–630 (high scale) <sup>†</sup>	n.a	
LiBr/H <sub>2</sub> O	AC	32	0.2 (low scale)	30 <sup>ad</sup> ; 80, 120 <sup>des</sup>	1.25	n.a	n.a	n.a	n.a	n.a	–/471.6 (80 °C, low scale)) <sup>†</sup>	n.a	
		42	0.3 (low scale)	30 <sup>ad</sup> ; 80, 120 <sup>des</sup>	1.25	n.a	n.a	n.a	n.a	n.a	–/669.6 (80 °C, low scale) <sup>†</sup> ; –/802.8 (120 °C, low scale) <sup>†</sup>	n.a	

(continued on next page)

**Table 3 (continued)**

Working pair													
Working pair													
Lithium compound/ Sorbate	Porous matrix	Li content [%]	Sorbate uptake [g/ g]	T [°C]	p [kPa]	λ [W/m K]	K <sub>p</sub> × 10 <sup>-12</sup> [m <sup>2</sup> ]	q [kW]	ε	Recovered heat [kJ]	ESD [kJ/kg/MJ/m <sup>3</sup> ]	Efficiency [%]	Ref.
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	−/182	n.a	[85]
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	−/200	n.a	[86]
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	−/273.6; −/342; −/334.8	n.a	[87]
LiOH-H <sub>2</sub> O/H <sub>2</sub> O	Ni-CNTs	14*; 23; 39; 100	n.a	30–120	2.97	3.78	n.a	n.a	n.a	n.a	3935/−	n.a	[96]
LiOH-H <sub>2</sub> O/H <sub>2</sub> O	CNs	50	n.a	20–120	2.97	1.95	n.a	n.a	n.a	n.a	2020/−	n.a	[94]
	MWCNTs	50	n.a	20–120	2.97	1.75	n.a	n.a	n.a	n.a	1804/−	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	[88]
	NaY-Z	80	n.a	30–200	2.98	n.a	n.a	n.a	n.a	n.a	1624/−	n.a	
LiOH-H <sub>2</sub> O/H <sub>2</sub> O	EG	85; 88; 92*; 95	0.641	105 <sup>c</sup> ; 30 <sup>d</sup>	2.55	6.52	1.2	n.a	0.6	n.a	1120/−	83.6	[75]
LiOH-H <sub>2</sub> O/H <sub>2</sub> O	GO	27.1	n.a	<200	2.55	1.8	n.a	n.a	n.a	n.a	1980/−	n.a	[92]
LiOH-H <sub>2</sub> O/H <sub>2</sub> O	EG	5; 8*; 12; 15	0.62; 0.64; 0.55; 0.49	30- 50 <sup>ad</sup> ; 120 <sup>des</sup>	1.23; 1.71; 2.34	n.a	n.a	n.a	n.a	n.a	~ 1000/−	n.a	[78]
Li <sub>4</sub> SiO <sub>4</sub> /CO <sub>2</sub>	Z	n.a	n.a	715	150	n.a	n.a	n.a	n.a	n.a	−/0.331–0.395 packed bed −/0.759–0.904 mat.	n.a	[89]
Li <sub>4</sub> SiO <sub>4</sub> /CO <sub>2</sub>	Z	n.a	n.a	700	100 <sup>car</sup> ; 10 <sup>dec</sup>	n.a	n.a	7.2 <sup>+</sup>	59	n.a	−/−	n.a	[90]
Li <sub>4</sub> SiO <sub>4</sub> /CO <sub>2</sub>	Z	n.a	n.a	~ 650	101 <sup>car</sup> ; 0 <sup>dec</sup>	n.a	n.a	>7.0 <sup>+</sup>	n.a	n.a	~ 450/−	n.a	[91]

Note: T –temperature of reaction; p –pressure; λ –thermal conductivity; K<sub>p</sub> –permeability; q –output power; ε –sorbent porosity; ESD –energy storage density; AC –activated carbon; ENG-TSA –expanded natural graphite treated with sulfuric acid; SS –silica solutions; EG –expanded graphite; AA –alumina; EVM –expanded vermiculite; VM –vermiculite; SG –silica gel; MWCNTs –multi-walled carbon nanotubes; WSS –wakkanai siliceous shale; <sup>c</sup> –charge; <sup>d</sup> –discharge; <sup>ad</sup> –adsorption; <sup>des</sup> –desorption; <sup>ST</sup> –short-term cycle; <sup>LT</sup> –long-term cycle; n.a. –not available. <sup>+</sup>value reported as kW per kilogram; <sup>†</sup> unit conversion; \*parameter selected by the authors for further testing.

Note: T –temperature of reaction; p –pressure; λ –thermal conductivity; K<sub>p</sub> –permeability; q –output power; ε –sorbent porosity; ESD –energy storage density; EG –expanded graphite; S-AA –silica-alumina; VM –vermiculite; Z –zeolite; GO –graphene oxide; Ni-CNTs –3D-nickel-carbon nanotubes; CNs –carbon nanospheres; MWCNTs –multi-walled carbon nanotubes; <sup>c</sup> –charge; <sup>d</sup> –discharge; <sup>ad</sup> –adsorption; <sup>des</sup> –desorption; <sup>car</sup> –carbonation; <sup>dec</sup> –decarbonation; n.a. –not available. <sup>+</sup>value reported as kW per kilogram; \*parameter selected by the authors for further testing.

#### 4.2.1. Expanded natural graphite (ENG-TSA) a matrix for TCS

This type of treated expanded graphite matrix is usually applied in order to test the capacity for several salts for heat storage applications. In this sense, Yu et al. [72,73] 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 thermal conductivity. 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 in terms of reaction 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 aiming for a 1 kWh lab-scale sorption prototype [73]. The results indicated that the whole experiment collected sorption heat of about 1496 kJ (0.42 kWh), achieving 80% of the predicted target of 1869 kJ (0.52 kWh), not fully achieving the expected target (1 kWh).

#### 4.2.2. Expanded graphite as matrix for TCS

Lithium compounds have also been used in conjunction with expanded graphite (EG) as a 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. [74], 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 873 Wh/kg (3142 kJ/kg) of composite sorbent. In the same way, Li et al. [75], developed a form-stable LiOH/EG composite and the thermochemical performance was investigated. They demonstrated that the sample with 8 wt% EG-doped (92% salt content) was the most promising, with a thermal conductivity of 6.52 W/(m K) and energy density of 1120 kJ/kg. Similarly, Myagmarjav et al. [76], 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 (Fig. 11).

#### 4.2.3. Silica gel as matrix for TCS

SG is one of the most commonly used sorbents since the mesoporosity of this compound facilitates the incorporation of the salt content whilst retaining easy access for the sorbate to the salt. Within the reviewed literature, SG has been used as a host matrix in conjunction with LiCl and LiBr. For instance, Tokarev et al. [82] studied the performance of the HeCol prototype –a novel adsorption cycle called “Heat from Cold”– with LiCl confined to the mesopores of the SG and methanol as the sorbate. Moreover, the effects of the heat source temperature and the rate of heat transfer fluid were also investigated. The results showed that at a heat source temperature of 20–30 °C, the sorbent allows a maximal temperature of 34–53 °C –suitable for warm floor and hot water systems. Also, a maximum specific heat power and sorbent heat capacity of 6.0–10.8 kW/kg and 620 kJ/kg were obtained respectively. This study concludes that the heat capacity reached by the sorbent is promising for designing the HeCol unit for upgrading the temperature of the ambient heat in cold countries. Similarly, Courbon et al. [83] synthesised and

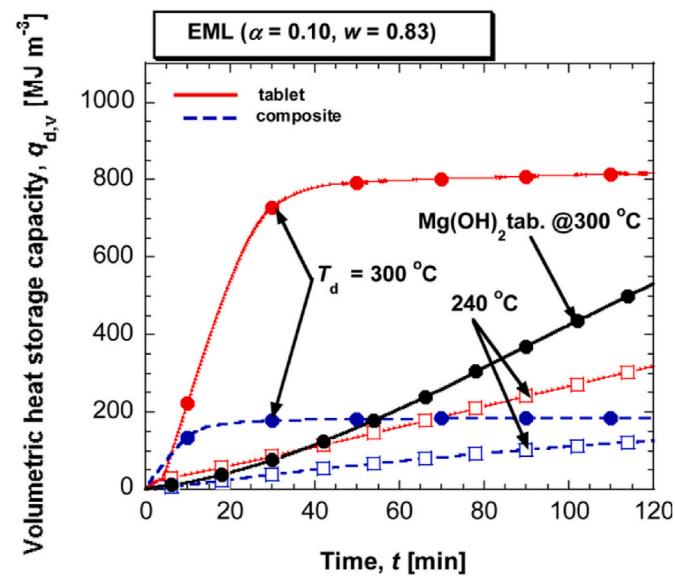


Fig. 11. Volumetric heat storage capacities of the EML tablet and composite [76].

characterised four different LiBr based composites with SG (37 wt% and 53 wt% SG/LiBr) and with AC (32 wt% and 42 wt% AC/LiBr) as the host matrices at a low scale (50 mg) and high scale (200 g). The results at low scale showed that SG/LiBr 53 wt% composite evidenced an exceptional energy storage density of 261 kWh/m<sup>3</sup> (939.6 MJ/m<sup>3</sup>, Table 3) at an adsorption and desorption temperature of 30 °C and 80 °C respectively, and a constant pressure of 12.5 mbar (1.25 kPa, Table 3). This same composite also had an energy storage density of 381 kWh/m<sup>3</sup> (1371.6 MJ/m<sup>3</sup>, Table 3) when the desorption temperature was increased from 80 °C to 120 °C. Regarding the higher scale, the SG/LiBr 53 wt% composite has a specific heat power of up to 286 W/kg (0.286 kW/kg, Table 3) and an energy storage density of 160–175 kWh/m<sup>3</sup> (576–630 MJ/m<sup>3</sup>, Table 3). Overall, the latest composite mixture is considered a promising alternative for heat storage in residential heating and water production applications.

#### 4.2.4. Vermiculite as matrix for TCS

Composite materials using LiCl, LiNO<sub>3</sub>, LiBr and 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. [80], 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 (4356 kJ/kg), and volume energy storage density of 171.61 kWh/m<sup>3</sup> (6178 MJ/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 with pure LiCl.

Vermiculite has also been assessed using other lithium salts. Casey et al. [84] evaluated the selection of hygroscopic salts and desiccant matrices as candidate materials for open thermal energy storage. Candidate materials selected were SG, Z, AC and 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 equilibrium moisture content (EMC) values up to 1.9 kg/kg. 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 time interval to reach equilibrium moisture content response time ( $T_{emc}$ ). Finally, the study concluded that the samples SIM-3a (CaCl<sub>2</sub>-VM), and SIM-3e (LiBr-VM) demonstrated very good potential to be used in an open TES system.

In a different approach, Sutton et al. [85] studied the hydration/dehydration of inorganic salts using CaCl<sub>2</sub> and LiNO<sub>3</sub> impregnated into porous VM. The study performed at high packing density showed that (during the discharge cycle) the performance of the two SIM materials (salt in a matrix) was significantly lower than that expected. However, when Sutton et al. [86] studied the interactions between common SIMs (salt in matrices) using CaCl<sub>2</sub>, LiNO<sub>3</sub>, MgSO<sub>4</sub> and vermiculite by using layering and blending techniques, the results showed that layering the CaCl<sub>2</sub> on the LiNO<sub>3</sub> gave a more efficient thermal release strategy and reached a thermal storage density of 0.2 GJ/m<sup>3</sup>. This research also emphasised that a significant reduction in efficiency may be due to improper mixing of the material.

#### 4.2.5. Zeolite as matrix for TCS

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. [88] synthesised lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O) by impregnation method with hygroscopic materials (where polyethylene glycol (PEG), lithium chloride LiCl, 13X-zeolite (13X-Z) and NaY-zeolite (NaY-Z) were chosen as hydrophilic promoters). The results revealed that LiOH·H<sub>2</sub>O/13X-Z presented the lowest apparent activation energy (21.5 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. [89], studied the reaction of Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub> for recovery and utilisation of the high-temperature produced from industrial processes. To do this, two reactors (Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub> packed bed reactor (LPR) 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 CO<sub>2</sub> pressure conditions, and the decarbonation process (thermal energy storage) was performed using a 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 (Fig. 12). The proposed Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub>/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 Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub>/zeolite as a TCS system, Takasu et al. [90] and Kim et al. [91] tested the same Li<sub>4</sub>SiO<sub>4</sub>/CO<sub>2</sub>/zeolite TCS system for high temperature performance. Takasu et al.'s [90] results indicated that carbonation of Li<sub>4</sub>SiO<sub>4</sub> was completed after 5 min, while decarbonation was completed after 150 min under isothermal experiments. In this case, the maximum  $w_{out}$  and  $w_{in}$  rates of Li<sub>4</sub>SiO<sub>4</sub> with 59% of porosity, were 7.2 kW/kg and 1.9 kW/kg, respectively. Meanwhile, Kim et al. [91] additionally developed tablet forms of Li<sub>4</sub>SiO<sub>4</sub> named K-tablets. The K-tablet showed a maximum thermal energy output rate of 9.82 kW/kg-tablet under 650 °C on the 10th cycle. Whilst, the thermal energy output rate for the pure powder was 3.25 kW/kg-Li<sub>4</sub>SiO<sub>4</sub> under the same reaction temperature.

#### 4.2.6. Graphene oxide as matrix for TCS

In order to expand the number of TCS applications, a comparative performance study for low-temperature TCS with LiOH·H<sub>2</sub>O and LiOH·H<sub>2</sub>O/GO was performed by Yang et al. [92]. Pure LiOH·H<sub>2</sub>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, LiOH reacted with water vapour very slowly (conversion of 35%, after 1 h with 511 kJ/kg). Thus, the enhancement of the hydration rate of LiOH is required for practical application. In this regard, LiOH·H<sub>2</sub>O nanoparticles (27.1 wt%) supported on GO obtained high heat storage density (1980 kJ/kg), due to the increase in surface area of nanoparticles in contact with the water molecules.

#### 4.2.7. Nanoparticles as matrix for TCS

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 the production of matrix materials since they exhibit large surface area, high thermal conductivity, low bulk density and chemical stability. The work done by Grekova [93] and Yang et al. [94] are good examples of the applications of carbon nanotubes (CNTs) and carbon nanospheres (CNSs) respectively. Grekova et al. [93] 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, LiCl·H<sub>2</sub>O and LiCl·2H<sub>2</sub>O, were formed due to water sorption on the LiCl-based composites. The water sorption capacity for both systems exceeded 1 g/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) – a term also referring to TCS, but specifically to sorption systems. 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. [94] studied the effect of carbon nanoadditives on LiOH·H<sub>2</sub>O-based composite for low temperature TCS. In this approach, CNSs and MWCNTs were used to modify LiOH·H<sub>2</sub>O. The results revealed that the composites LiOH·H<sub>2</sub>O/CNSs and LiOH·H<sub>2</sub>O/MWCNTs exhibited higher heat storage densities (i.e. 2020 and 1804 kJ/kg respectively) compared with pure LiOH·H<sub>2</sub>O (i.e. 661 kJ/kg) (Fig. 13). 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.

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 a solid matrix, they usually fail because of the degradation, agglomeration and low thermal conductivity amongst other things.

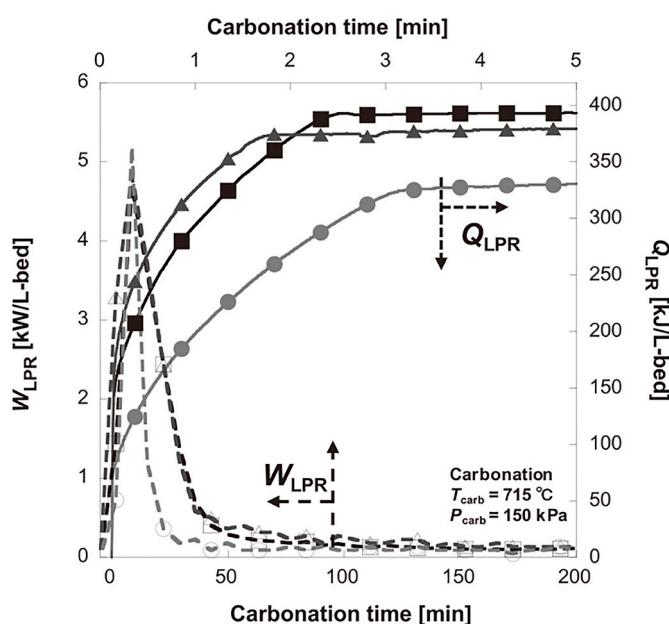
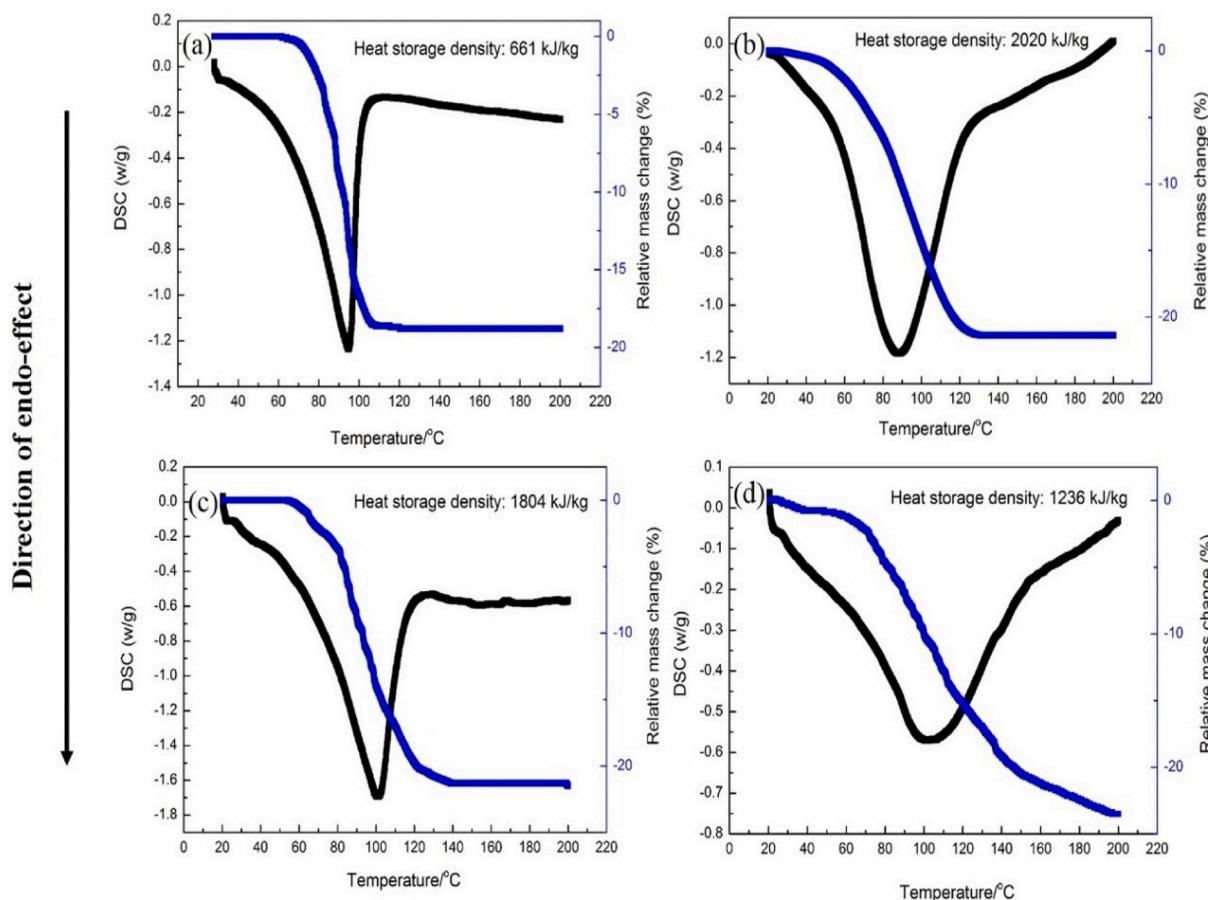


Fig. 12. Thermal energy output capacity and output rate for LPR bed [89].



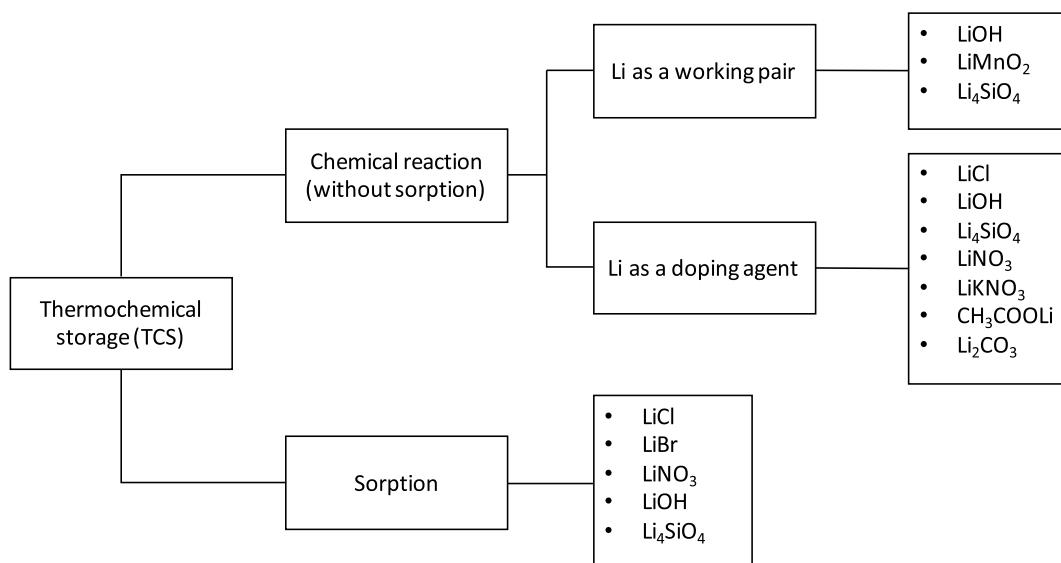
**Fig. 13.** TG-DSC curves of as-synthesised samples: (a) LiOH pure, (b) LiOH/CNSs, (c) LiOH/MWCNTs, and (d) LiOH/AC after 1 h of hydration [94].

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.

Fig. 14 summarises the main lithium-containing salts applied in TCS systems based on chemical reactions and sorption mechanisms for heat

storage.

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. When AC is mixed with EG, the matrix produced had a thermal



**Fig. 14.** Summary of Lithium-containing compounds used for chemical reactions and sorption.

conductivity of 76.46 W/m K [77], and when mixed with ENG-TSA values between 2.0 and 2.8 W/m K were observed [72,73]. This value indicates the ability of the matrix 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 4356 kJ/kg [80]. This value indicates the amount of energy the matrix 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 25 research documents in total based on lithium salts.

## 5. Technological patents utilising lithium compounds for TCS

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. 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 growth with new products and processes, establishing renewed employments positions and protecting the environment and its resources [97]. In the context of technology management, the early detection of recent trends in technical improvement is of essential interest for investors and companies [98].

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 [99–107], industrial waste [108], solar energy [109–113] and mixed sources [114–121]. Several patents are related to the use of off-peak electricity and the safety of thermal power [99,100,105,120], in this way energy consumption and costs are diminished. Many applications were proposed, the most significant were carbonising systems employed in the treatment of sludge and garbage [101], energy supply system for hospitals [104], industrial waste heat recovery [108], automotive solar energy [116] and a device applied to molten salt storage for solar-thermal power generation [121]. A path to optimise TES systems is blending different energy sources, such as solar energy with waste heat [117,121] or with electric power [119,120]. 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 [118].

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 [122] and by a covalent organic framework material (COF) in the other method [123]. Both methods considered storage of the heat energy through the 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 achieve high-density storage of 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 [122,123].

## 6. Hints into the future trends of Li-based 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 commercialisation of this technology will require 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, the potential toxicity of material amongst other things. Such technology could then be deployed for industrial and social activities so waste heat can be recovered and reused with limited generation of waste energy.

Current and future trends targeted at improving TCS materials are effectively looking at the nanoscale. Changing 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 [93]. 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 –a parameter that can be improved by reducing salt agglomeration–, iv) lifetime of the matrix –performance maintenance by avoiding the system's degradation over time. For instance, in more complex devices such as heat-pumps or refrigeration, the application of matrix materials has been crucial for continued improvement of system performance, especially aspects related to the capacity of a system to transfer heat in and out (i.e. permeability and thermal conductivity) and ways of improving the lifetime –number of cycles– of such units. These aspects will ultimately have an impact on 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 is employing salts with sufficient capacity to store energy. The challenges of working with salts are to address variables related to 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). One mechanism 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

**Table 4**

Patents related to the use of LiBr for refrigeration.

Energy source	Specifications	The invention	LiBr application system	Observations	Reference
Electric power	Off-peak electricity	A thermal storage and energy accumulation conversion device	LiBr refrigerator	Applied through electricity to store energy and uses it at peak times	[99]
	Steam power plant	A soil source cold storage and heat storage system device	LiBr absorption heat pump unit	Use renewable air to store cold in winter and spring to increase the available cold in summer	[100]
	Heat and electricity generators	Carbonisation system of sludge and garbage	LiBr refrigeration station	It can simultaneously provide combined cooling, heat, and power for a city and treat sludge and garbage	[101]
	Electric heater	A molten salt energy storage cold and heat combined supply device	LiBr absorption heat pump unit	The low temperature molten salt storage tank is connected with a high temperature molten salt storage tank through a molten salt electric heater	[102]
	Electrical output of gas turbine generator group	A cooling heating and power triple co-generation peak shaving system	Combined solar LiBr absorption air conditioning system		[103]
	Gas turbine	A hospital integrated energy supply system based on gas turbine	LiBr steam type refrigerating unit		[104]
	Off-peak electricity and thermal power	A device that takes into account the safety of the thermal power air condenser and the power peak regulation	A LiBr unit	For solving the problems of thermal power air cooling units in summer and system day and night peak shaving	[105]
	Internal combustion engine arrangement	A system for cooling the intake air of the internal combustion engine by using the water of the cylinder jacket of the internal combustion engine	Uses water as a refrigerant and a solution of LiBr as an absorbent for refrigeration	The jacket water in the cylinder of the internal combustion engine device serves as the heat source for the LiBr units	[106]
	Gas engine	A heating and cooling balance structure capable of stabilising the load of a gas turbine in a gas distributed energy station	LiBr absorption type refrigerating unit	The LiBr refrigerator and the thermal storage flash water tank are connected through the LiBr heating steam pipeline	[107]
	Waste heat recovery from the malt industry	Malt cooking waste heat utilisation system with heat storage function	LiBr absorption refrigeration unit		[108]
Industrial waste Solar energy	A solar thermal collector	A solar heating and cooling system	LiBr refrigerator		[109]
		An intelligent solar air-conditioning system	LiBr heat pump unit	It solves the technical problems of using solar energy to heat buildings in winter and cool in summer	[110]
		A solar energy power generation light field system		Integrates an 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	[111]
		A solar double-effect absorption heat pump drying system with thermal storage function			[112]
	Solar photo-thermal technologies	A combined solar LiBr absorption air conditioning system	Organically combines heat pump energy conservation technology and solar photo-thermal technology	The heat transfer oil in the solar collector is used as the heat source, and the LiBr absorption heat pump unit produces hot air for drying operations	[113]
	Solar thermal energy steam type heat collector	A solar thermal energy steam type refrigerating system		Reduce the instability of single energy supply, and can realise the functions of cooling, heating, and hot water.	[114], [115]
	Photo-thermal power generation	A device for utilising molten salt energy storage for distributed energy utilisation, and belongs to the technical field of photo-thermal power generation		To satisfy ambient temperature requirements such as office space or operation control rooms	[121]
	Solar energy and engine waste heat	A dual-energy refrigeration air conditioner with solar energy and engine waste heat for automobiles		Utilises solar energy and engine waste heat energy in automobile air conditioners	[116]
	Solar and geothermal energies	A composite energy supply system coupled with a solar thermal system and a ground source heat pump system		Realises the complementary advantages of the two renewable energy sources and further improves the energy utilisation rate of the system.	[117]
	Solar energy and electric power (solar heat collector and generator)	A combined energy based solar LiBr absorption trigeneration system	Organically combines heat pump energy conservation technology and solar photo-thermal technology	It can reduce the instability of a single power supply and can achieve cooling, heat supply and hot water supply functions	[118]
Mixed sources	Solar, electric-thermal energies	A multi-energy complementary cooling and heating system, which includes a solar hot water system		The model uses a solar hot water system and an electric heat storage boiler for heating in winter	[119]
					[120]

(continued on next page)

**Table 4 (continued)**

Energy source	Specifications	The invention	LiBr application system	Observations	Reference
Solar energy, waste heat recovery and electrical power (solar heat collector, and an electricity storage power source)	Solar energy, 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	

temperature of reaction whilst maintaining the energy density of the original salt. The application of different lithium salts has shown to be an alternative approach to improving the application of TCS systems across a broader range of reaction temperatures.

Another attractive future application for Li compounds is their use in TCS systems incorporated into concentrating solar power (CSP) plants with lower cost photovoltaic plants. This mixed system was proved to heighten dispatchability and solar-to-electricity efficiency, and utilises synergies related to dispatchability and costs. Three studies were recently developed related to multi-objective optimizations and guidelines for the design of hybrid CSP plants with a calcium-looping TCS system, under different solar sources: Tonopah (United States), Seville (Spain), and the Atacama Desert (Chile). The Atacama Desert resulted the best solar resource, with a capacity factor of 73% and the average cost of electricity close to 123 USD·MWh<sup>-1</sup> [124]. These guidelines provide a preliminary design for reasonably priced and dispatchable hybrid CSP plants, and similar research could be further performed with lithium compounds, such as LiCl or LiOH. However, multi-objective optimisation will be further required to achieve an optimal hybrid system and to understand the interactions and synergies between these different technologies.

Lastly, one important aspect that needs to be urgently addressed for TCS systems to reach full applicability is the high cost of their implementation, especially associated with the (limited) availability of components in high demand, such as lithium salts. The high value of lithium salts is mainly associated with the purification process of the targeted elements and depends on the complexity of the mixture [125]. In this context, by-products and wastes from the mining industry represent a 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  $<100^\circ\text{C}$  [126]) which certainly hampers potential applications as TCS systems [127]. 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 system.

## 6.2. Environmental challenges

Along with the technological and economic challenges, it is necessary to solve and minimise the environmental impacts that TCM systems cause. Few TCS studies were carried out to quantify the environmental impact in terms of Global Warming Potential (GWP) or quantify CO<sub>2</sub> equivalent emissions. Masruroh et al. [128] applied a life cycle methodology to analyse a new solar heating/cooling system's environmental impact coupled with a TCS unit (SOLARSTORE), from raw material acquisition to waste disposal. The study considered four phases; the first was "Raw material acquisition and components manufacturing", the second one was "Transportation of raw materials to manufacturing site",

and the last two were related to transportation of SOLARSTORE to Spain and France, respectively. The results of life cycle analysis (LCA) showed that Phase 1, of raw materials and manufacturing, contribute 99% to the total environmental impacts (6.3–10 kg CO<sub>2</sub> equivalent, 46.6–70 g SO<sub>2</sub>, 2.1–3.1 g phosphate and 0.99–2.2 g C<sub>2</sub>H<sub>4</sub>) during the whole life cycle. In this sense, the use of thermal storage materials with a low carbon footprint could benefit new solar systems with TCS and reduce their environmental impact.

The supply of materials based on lithium compounds, reviewed in this paper and in general, comes mainly from two production processes: a) leaching of spodumene rock, concentration and chemical conversion [129], and b) from brines from the "lithium triangle" [130], where Chile is the majority producing country. In this process, the brines are pumped from under the salt crust in different salt flat areas and deposited in solar evaporation ponds for subsequent concentration of the brine up to 6% of Li content. The solar evaporation production step, with high evaporation rates (3200 mm/year), is used to precipitate the inorganic salts. For this reason, these compounds are considered as low carbon footprint materials. Additionally, several by-products and wastes from the nonmetallic mining, such as salt hydrates and double salts, are available but have reduced or almost no applications, accumulating and aggravating environmental pollution [131]. The use of these substances as thermal energy storage materials is increasing in interest. Their low cost is close to zero, and these could be considered zero carbon footprint materials since they are already accumulated, with low embodied energy.

By-products and wastes from mining industries could therefore 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 represents an additional economic value and 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 lithium's mining activity 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, an activity that inherently has environmental impacts. Although obtaining lithium compounds through solar evaporation could be considered a sustainable process that produces low-carbon footprint materials, it is essential to mention that the water footprint must also be taken into account for a more objective analysis of the real environmental impact. For example, non-metallic mining in Chile occurs in the Atacama desert, the driest desert in the world, where production of one ton of lithium compound requires more than half a million gallons of brine [129]. In other terms, the water footprint must be estimated as well as the carbon footprint of the TCM storage media. The release of the LCA data in terms of GWP and water footprint could drive more drastic technological change. This environmental duality is a signal to look for different strategies, and thus wastes and synthetic materials could potentially serve as a way to overcome unwanted environmental externalities [132].

TCS systems offer the potential of highly compact and energy dense storage systems that experience minimal energy loss and can be tuned to an application's thermal requirements. They effectively provide an attractive mechanism for the reduction of energy losses and consequently, the reduction of the environmental stress derived from the

process of energy generation. The current climate emergency calls the scientific community to strengthen its efforts to develop more and better alternatives for more energy-efficient technologies and to aim at reducing the impact of industries and other human activities upon the environment [133].

## 7. Conclusions

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

Thus, using a semiautomated screening approach from scientific databases it was possible to evidence the following:

- o A comprehensive search and analysis of the available literature highlighted that most research that has been conducted into the application of lithium compounds in TCS systems has previously focused on sorption systems. Literature relating to TCS systems utilising lithium compounds in thermochemical reactions is less common.
- o Published research relating to the use of lithium compounds in TCS systems based on chemical reactions mostly apply lithium as a secondary component or dopant. In these papers, lithium salts were used to change the activation energy and reaction temperatures of other salts, modifying their properties for particular applications.
- o 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 development of these salt-matrix composites is fundamental to establishing an effective TCS system and is a key topic for many research papers.
- o 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 and related to LiH used as the energy storage system.
- o The papers and patents reviewed in this work used a wide variety of different measures to assess the performance of the system being developed. The use of different units and measures across the published work not allow like-for-like comparison results. Here we suggest the need for systematisation in reporting critical data to facilitate a common understanding with regards to the advances in energy storage, especially when referring to heat storage density.

## Funding

Authors acknowledge to ANID/FONDAP N° 15,110,019, CONICYT/PCI/REDES N°170131 projects. Paula E. Marín would like to thank the National Agency for Research and Development (ANID)/Scholarship Program/Postdoctorado en el Extranjero Becas Chile/2019-74200057. Yanio Milian would like to thank ANT1885, CORFO 16ENI2-71940 INGENIERIA2030 and Postdoctoral/FONDECYT N° 3200786 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. The authors would like to acknowledge the support of InnovateUK through their funding of T-ERA facilities at the University of Warwick.

## Declaration of competing interest

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

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rser.2021.111381>.

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