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

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Abstract

Keywords: lithium compounds; thermochemical storage; patents; technological and cost challenges; energy storage density; TCS operational conditions.
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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$_2$ and water [22], the cyclical behaviour of MgSO$_4$ and its dehydration [23], the storage of thermal energy based on Ca(OH)$_2$ 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 Mg(OH)₂ and LiCl-modified Mg(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].

![Bar chart showing distribution of lithium applications]

**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].

\[ A + \text{heat} \Leftrightarrow B + C \]  

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$^3$) 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 Science. 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], LiMnO₂ [58,59], and Li₄SiO₄ [60]. Reactions were tested with different working pairs, for instance O₂ and CO₂ 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 H₂ 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 (Li$_4$SiO$_4$/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 Li$_4$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 Li$_4$SiO$_4$ were sufficient for use as TCS material at around 700 °C (Figure 8). Furthermore, the results indicate that by regulating the CO$_2$ pressure, the temperature for heat storage and heat output could be controlled.

![Figure 7. Cyclical oxidation/reduction of LiMnO$_2$ in the 800 – 1000 °C temperature range](image)

[58].
Figure 8. Durability of Li$_4$SiO$_4$ reactivity observed at 700 ºC. (b) Comparison of carbonation and (c) decarbonation reaction [60].

Table 1. Lithium compounds used as working pair.

<table>
<thead>
<tr>
<th>Lithium compound</th>
<th>Working pair</th>
<th>Reactions</th>
<th>$\Delta H$ [kJ/mol]</th>
<th>$T$ [ºC]</th>
<th>$q_v$ [kJ/L]</th>
<th>$q_g$ [kJ/kg]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>LiOH/Li</td>
<td>2LiOH(s) + 2Li(l) → 2Li$_2$O(s) + H$_2$(g)</td>
<td>-232</td>
<td>500</td>
<td>n.a</td>
<td>n.a</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2Li$_2$O(s) → Li$_2$O$_2$(s) + 2Li(g)</td>
<td>883</td>
<td>800</td>
<td>n.a</td>
<td>n.a</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li$_2$O$_2$(s) + H$_2$O(l) → 2LiOH(s) + 1/2O$_2$(g)</td>
<td>-51</td>
<td>300</td>
<td>n.a</td>
<td>n.a</td>
<td></td>
</tr>
<tr>
<td>LiMnO$_2$</td>
<td>LiMnO$_2$/O$_2$</td>
<td>3LiMnO$_2$(s) + 1/2O$_2$(g) → 2LiMnO$_2$(s) + 1/2O$_2$(g)</td>
<td>21(ox); 25(red)</td>
<td>800-1000</td>
<td>n.a</td>
<td>n.a</td>
<td>[58]</td>
</tr>
</tbody>
</table>
Lithium has not only been used as the main reactant component (i.e. working pair). In fact, there is 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\(^-\)) bond-braking from calcium hydroxide (Ca(OH)\(_2\)) [61]. Additionally, lithium doping has been shown to promote the process of carbonation, an effect shown by Shkatulov et al. [62] where applying salts of lithium acetate (CH\(_3\)COOLi) and lithium potassium nitrate (Li\(_{0.42}\)K\(_{0.58}\)NO\(_3\)) increased the carbonation conversion, enhancing the process of heat storage.

The lithium salts used as dopants are listed in Table 2. As can be seen in the table, the main doping lithium-based salts are LiCl [63,64], LiOH [61,64], LiNO\(_3\) [65,66], Li\(_4\)SiO\(_4\) [67] and

<table>
<thead>
<tr>
<th>Chemical 1</th>
<th>Chemical 2</th>
<th>ΔH</th>
<th>T (°C)</th>
<th>q(_v) (kWh/m(^3))</th>
<th>q(_g) (kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMnO(_2)</td>
<td>LiMnO(_2)/O(_2)</td>
<td>37</td>
<td>700</td>
<td>n.a</td>
<td>n.a</td>
</tr>
<tr>
<td>Li(_4)SiO(_4)</td>
<td>Li(_4)SiO(_4)/CO(_2)</td>
<td>-94</td>
<td>650-700</td>
<td>750(^\dagger)</td>
<td>780(^\dagger)</td>
</tr>
</tbody>
</table>

Note: ΔH – Heat of reaction; T – temperature of reaction; q\(_v\) – volumetric thermal energy density; q\(_g\) – gravimetric thermal energy density; n.a. – not available. \(^\dagger\)used in TCS, \(^\ddagger\)used in chemical heat pump (CHP).
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)$_2$ 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)$_2$ 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 ºC 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$_3$/Mg(OH)$_2$)$_Y$ (where Y is the LiNO$_3$ content). The results indicate that lithium salt diminished the dehydration start temperature by 76 ºC in the final material; while the reaction heat remained almost unaffected below 5 wt.% of lithium salt content. The LiNO$_3$-doped Mg(OH)$_2$ was able to store up to 800 – 1000 kJ/kg at a temperature below 235 ºC (with a water vapour pressure of 2.3 kPa).
of the dehydration peak depends on Y: the higher the Li salt content, the lower the peak temperature (Figure 9).

Similarly, lithium compounds have also been used to study the effect of doping in carbonation/decarbonation reactions. Skatulov et al. [62] adapted the MgO/CO$_2$ working pair to promote the TCS dynamics at medium temperatures, studying the carbonation kinetics of Li$_{0.42}$K$_{0.58}$NO$_3$/MgO, the de-carbonation kinetics of Li$_{0.42}$K$_{0.58}$NO$_3$/MgCO$_3$ and the cycling stability of the composite. The work demonstrated that the de-carbonation process can be carried out at T > 330 °C, and that the heat storage capacity of the doped salt 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 MgO/CO$_2$ working pair to study the effect of doping with (LiK)NO$_3$. To do this, a number of carbonation dynamic experiments were carried out. The results showed that at $T_{\text{carb}}$ of 350 °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 ºC (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$_3$/MgO [62].

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

**Table 2.** Lithium compounds used as doping element.
<table>
<thead>
<tr>
<th>Lithium Compound</th>
<th>Working Pair</th>
<th>Reaction</th>
<th>ΔH [kJ/mol]</th>
<th>T [°C]</th>
<th>(Q_{total} ) [kJ/kg]</th>
<th>q_v [kJ/L]</th>
<th>q_g [kJ/kg]</th>
<th>p [kPa]</th>
<th>Energy Barrier [eV]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>MgO/H_2O</td>
<td>MgO(s) + H_2O(g) ↔ Mg(OH)_2(s)</td>
<td>-81</td>
<td>300 (dehydration) 110-200 (hydration) 1400 (100°C) 724 (180°C)</td>
<td>57.8 (H_2O)</td>
<td>n.a</td>
<td>n.a</td>
<td>5.78</td>
<td>[63]</td>
<td></td>
</tr>
<tr>
<td>LiOH · H_2O</td>
<td>CaO/H_2O</td>
<td>CaO(s) + H_2O(g) ↔ Ca(OH)_2(s)</td>
<td>109.3</td>
<td>430 (dehydration)</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>0.1</td>
<td>[61]</td>
</tr>
<tr>
<td>Li_4SiO_4 /CO_2</td>
<td>Li_4SiO_4(s) + CO_2(g) ↔ Li_2CO_3(s) + Li_2SiO_3(s)</td>
<td>-94</td>
<td>800</td>
<td>n.a</td>
<td>51</td>
<td>n.a</td>
<td>100 (carbonation, CO_2)</td>
<td>n.a</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>LiNO_3/H_2O</td>
<td>MgO/H_2O</td>
<td>Mg(OH)_2(s) ↔ MgO(s) + H_2O(g)</td>
<td>81</td>
<td>&lt;235 (dehydration) 800-1000</td>
<td>n.a</td>
<td>n.a</td>
<td>2.3</td>
<td>n.a</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>LiNO_3/H_2O</td>
<td>MgO/H_2O</td>
<td>Mg(OH)_2(s) ↔ MgO(s) + H_2O(g)</td>
<td>81</td>
<td>90-150 (hydration) 290-1024</td>
<td>n.a</td>
<td>n.a</td>
<td>16.7-33.5 (H_2O)</td>
<td>n.a</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>LiKNO_3/CH_3C_0O_3Li</td>
<td>MgO/CO_2</td>
<td>MgCO_3(s) ↔ MgO(s) + CO_2(g)</td>
<td>116.4</td>
<td>&gt;330 (decarbonation) 280-360 (carbonation)</td>
<td>n.a</td>
<td>16</td>
<td>160</td>
<td>0-100 (CO_2)</td>
<td>n.a</td>
<td>[62]</td>
</tr>
<tr>
<td>LiKNO_3/CO_2</td>
<td>MgO(s) + CO_2(g) ↔ MgO(s)</td>
<td>~400 (carbonation)</td>
<td>1180-1250</td>
<td>n.a</td>
<td>n.a</td>
<td>50–101(CO_2)</td>
<td>n.a</td>
<td>[68]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MgCO$_3$(s)  300-350 (decarb onation)      
| LiCl | CaO/ LiOH | CaO(s) | - | 350 | 450-670 n.a n.a 7.4 n.a | [64] |
| LiOH | H$_2$O    | H$_2$O(g) | 4 | 104 | (dehyd ration) |
| Li$_2$C | H$_2$O(g) | ↔Ca(O H)$_2$(s) | 110 | (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)
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 ºC 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/H₂O 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$^3$ 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)$_2$ 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$^3$(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].](image)

Composite materials using LiCl, LiNO$_3$, 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 ºC. 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/m³. 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 CaCl₂, MgSO₄, Ca(NO₃)₂, LiNO₃ and LiBr as salts. The N₂ 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 (CaCl₂-VM), SIM-3c (Ca(NO₃)₂-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(NO₃)₂-VM) was discarded because it showed an abrupt reduction in the potential performance because of its large T_{emp} response time. Finally, the study concluded that the samples SIM-3a (CaCl₂-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 CaCl₂ and LiNO₃ 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 CaCl₂, LiNO₃, MgSO₄ and vermiculite by using layering and blending techniques, the results showed that layering the CaCl₂ on the LiNO₃ gave a more efficient thermal release strategy and reached a thermal storage density of 0.2 GJ/m³. 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 (LiOH·H₂O) 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·H₂O/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. [83], studied the reaction of Li$_4$SiO$_4$/CO$_2$ for recovery and utilisation of the high-temperature produced from industrial processes. To do this, two reactors (Li$_4$SiO$_4$/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 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 Li$_4$SiO$_4$/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 Li$_4$SiO$_4$/CO$_2$/zeolite as a TCS system, Takasu et al. [84] and Kim et al. [85] tested the same Li$_4$SiO$_4$/CO$_2$/zeolite TCS system for high temperature performance. Takasu et al’s [84] results indicated that carbonation of Li$_4$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 Li$_4$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 Li$_4$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 10th cycle. Whilst, the thermal energy output rate for the pure powder was 3.25 kW/kg- Li$_4$SiO$_4$ under the same reaction temperature.
In order to expand the number of TCS applications, a comparative performance study for low-temperature TCS with LiOH·H₂O and LiOH·H₂O/graphene oxide (GO) was performed by Yang et al. [86]. Pure LiOH·H₂O showed an endothermic heat about 1460 kJ/kg at 65 ºC, with dehydration starting at around 60 ºC and finishing at 98 ºC. Nonetheless, LiOH reacted with water vapour very slowly (35% even after 1 h, with 511 kJ/kg). Thus, the enhancement of hydration rate of LiOH is required for practical application. In this regard, LiOH·H₂O 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

**Figure 14.** Thermal energy output capacity and output rate for LPR bed [83].
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, LiCl·H₂O and LiCl·2H₂O, were formed due to water sorption on the LiCl-based composites. The water sorption capacity for the 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). 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 LiOH·H₂O-based composite for low temperature TCS. In this approach, carbon nanospheres (CNSs) and multi-walled carbon nanotubes (MWCNTs) were used to modify LiOH·H₂O. 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 LiOH·H₂O/CNSs and LiOH·H₂O/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 has 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.
Table 3. Lithium compound used in sorption applications.

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<td>LiCl H2O AC</td>
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<td>0.97</td>
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<td>50 (cha); 40 (dis)</td>
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<td>3.43</td>
<td>0.80</td>
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<td>874 (consolidated sorbent)</td>
<td>2622 (LiCl)</td>
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<td>[70]</td>
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<td>120 (cha)</td>
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<td>5.3;</td>
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<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>273.6</td>
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<tr>
<td>LiOH·H₂O</td>
<td>Ni-CNTs</td>
<td>n.a</td>
<td>30-120</td>
<td>2.97</td>
<td>3.7</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>3935</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[83]</td>
<td></td>
<td></td>
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<tr>
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<td>CNs</td>
<td>50</td>
<td>n.a</td>
<td>20-120</td>
<td>2.97</td>
<td>1.9</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>2020</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[84]</td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>MWCNTs</td>
<td>50</td>
<td>n.a</td>
<td>20-120</td>
<td>2.97</td>
<td>1.7</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>1804</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
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<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>13X-Z</td>
<td>80</td>
<td>n.a</td>
<td>30-200</td>
<td>2.98</td>
<td>n.a</td>
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<td>n.a</td>
<td>n.a</td>
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<td>n.a</td>
<td>n.a</td>
<td>[86]</td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>NaY-Z</td>
<td>80</td>
<td>n.a</td>
<td>30-200</td>
<td>2.98</td>
<td>n.a</td>
<td>n.a</td>
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<td>n.a</td>
<td>n.a</td>
<td>1624</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[87]</td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>EG</td>
<td>85; 88; 92°;</td>
<td>0.64</td>
<td>2.55</td>
<td>6.5</td>
<td>1.2</td>
<td>n.a</td>
<td>0.6</td>
<td>n.a</td>
<td>1120</td>
<td>n.a</td>
<td>n.a</td>
<td>83.6</td>
<td>[88]</td>
<td></td>
<td></td>
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<tr>
<td>LiOH·H₂O</td>
<td>GO</td>
<td>27.9</td>
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<td>&lt;200</td>
<td>2.55</td>
<td>1.8</td>
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<td>n.a</td>
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<td>n.a</td>
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<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[89]</td>
<td></td>
</tr>
<tr>
<td>Li₄SiO₄</td>
<td>CO₂</td>
<td>n.a</td>
<td>n.a</td>
<td>715</td>
<td>150</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>331-395</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[90]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>CO₂</td>
<td>Z</td>
<td>n.a</td>
<td>n.a</td>
<td>700</td>
<td>100(c</td>
<td>n.a</td>
<td>n.a</td>
<td>7.2</td>
<td>59</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[84]</td>
<td></td>
</tr>
<tr>
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<td></td>
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<tr>
<td>Li₄SiO₂CO₂Z</td>
<td>n.a</td>
<td>n.a</td>
<td>~650</td>
<td>101(c</td>
<td>n.a</td>
<td>n.a</td>
<td>&gt;7</td>
<td>n.a</td>
<td>n.a</td>
<td>~450</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
<td>[85]</td>
<td></td>
</tr>
</tbody>
</table>

Note: T – temperature of reaction; p – pressure; λ – thermal conductivity; Kₚ – permeability; q – output power; ε – sorbent porosity; AC – activated carbon; ENG-TSA – expanded natural graphite treated with sulfuric acid; SS – silica solutions; EG – expanded graphite; AA – alumina; S-AA – silica-alumina; EVM – expanded vermiculite; VM – vermiculite; Z – zeolite; SG – silica gel; GO – graphene oxide; Ni-CNTs – 3D-nickel-carbon nanotubes; CNs – carbon nanospheres; MWCNTs – multi-walled carbon nanotubes; WSS – wakkanai siliceous shale; cha – charge; dis – discharge; ad – adsorption; des – desorption; ST – short-term cycle; LT – long-term cycle; car – carbonation; dec – decarbonation; n.a. – not available. † - value reported as kW per gram; * - parameter selected by the authors for further 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/H₂O, 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/H₂O 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.

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Specifications</th>
<th>The invention</th>
<th>LiBr machine</th>
<th>Observations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric power</td>
<td>Off-peak electricity</td>
<td>A thermal storage and energy accumulation conversion device</td>
<td>LiBr refrigerator</td>
<td>Stores energy by off-peak electricity, uses the energy at the high peak</td>
<td>[93]</td>
</tr>
<tr>
<td>Steam power plant</td>
<td>A soil-source cold-storage heat accumulation system</td>
<td>The refrigeration unit in the refrigeration system can be driven by thermal energy, such as a LiBr refrigeration unit</td>
<td></td>
<td>Hot peak regulation usefulness of steam power plant, to draw the heat that stores during winter</td>
<td>[94]</td>
</tr>
<tr>
<td>Heat and electricity generators</td>
<td>A sludge and garbage carbonising system</td>
<td>LiBr refrigerating machine room</td>
<td></td>
<td>Can simultaneously provide combined cooling, heat and power for a city and treat sludge and garbage</td>
<td>[95]</td>
</tr>
<tr>
<td>Electric heater</td>
<td>A cold and hot antithetical couplet of fused salt energy storage supplies device</td>
<td>LiBr absorption heat pump unit</td>
<td></td>
<td>Fused saltwater steam generator with parallely connected respectively between the steam user have steam water heat exchanger</td>
<td>[96]</td>
</tr>
<tr>
<td>Electrical output of gas turbine generator group</td>
<td>A cooling heating and power triple co-generation peak shaving system</td>
<td>The combined solar LiBr absorption air conditioning system</td>
<td></td>
<td></td>
<td>[97]</td>
</tr>
<tr>
<td>Gas turbine</td>
<td>An energy supply system synthesises in hospital based on gas turbine</td>
<td>LiBr steam type refrigerating unit</td>
<td></td>
<td></td>
<td>[98]</td>
</tr>
<tr>
<td>Off-peak electricity and aestivation</td>
<td>A device considering safe aestivation and electric power peak-load regulation of a thermal power air cooled condenser</td>
<td>A LiBr unit</td>
<td></td>
<td>For solving the problem of safe aestivation of a thermal power air cooled unit.</td>
<td>[99]</td>
</tr>
<tr>
<td>Internal combustion engine arrangement</td>
<td>An internal - combustion engine cylinder liner water cooling internal - combustion engine to admit air</td>
<td>Uses water as a refrigerant and a solution of LiBr as an absorbent for refrigeration</td>
<td></td>
<td>The cylinder liner water in the internal - combustion engine arrangement used as heat source for the LiBr units</td>
<td>[100]</td>
</tr>
<tr>
<td>Category</td>
<td>Description</td>
<td>Additional Details</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas engine</td>
<td>A heat and cold supply balance structure capable of stabilising the load of a gas turbine for a gas distributed energy station</td>
<td>LiBr absorption type refrigerating unit is linked to the heat storage flash evaporation water tank through a LiBr heating steam pipeline</td>
<td>[101]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial waste</td>
<td>Waste heat recovery from malt industry</td>
<td>A malt waste heat utilisation system of cooking with heat-retaining function</td>
<td>[102]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar energy</td>
<td>A solar thermal collector</td>
<td>A solar heating and refrigerating system</td>
<td>A cooling water pump was employed</td>
<td>[103]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>An intelligent solar air-conditioning system</td>
<td>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</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A solar energy power generation light field system</td>
<td></td>
<td>[105]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A solar double-effect absorption heat pump drying system with the thermal storage function</td>
<td>Hot wind is prepared by the LiBr unit for drying operation</td>
<td>[106]</td>
<td></td>
</tr>
<tr>
<td>solar photo-thermal technologies</td>
<td>A combined solar LiBr absorption air conditioning system</td>
<td>It can have refrigerating, heat supply and hot water supply functions</td>
<td></td>
<td>[107]</td>
<td></td>
</tr>
<tr>
<td>Solar energy (solar thermal energy steam type heat collector)</td>
<td>A solar thermal energy steam type refrigerating system</td>
<td>To satisfy ambient temperature requirements such as office space or operating control room</td>
<td></td>
<td>[108,109]</td>
<td></td>
</tr>
<tr>
<td>Photo-thermal power generation</td>
<td>A device and method for performing distributed energy utilisation on</td>
<td></td>
<td></td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>Mixed sources</td>
<td>Solar energy and engine waste heat</td>
<td>A solar photo-thermal system and ground source heat pump system coupled composite energy supply system</td>
<td>Complementation of advantages of the two renewable energy sources was achieved</td>
<td>[112]</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
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<td>-------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Solar energy and electric power (solar heat collector and a generator)</td>
<td>A combined energy-based solar LiBr absorption trigeneration system</td>
<td>Can reduce the instability of single energy supply, and can achieve cooling, heat supply, and hot water supply functions</td>
<td>[113]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar, electric-thermal energies</td>
<td>A cooling and heating system, which provide multiple forms of energy to complement each other</td>
<td>Utilize solar water heating system and electric thermal storage boiler heating winter</td>
<td>[114]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar energy, waste heat recovery and electrical power (solar heat collector, and an electricity storage power source)</td>
<td>A waste heat recovery type off-peak electricity energy storage heating system</td>
<td>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</td>
<td>[115]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 (LiCl·MgCl₂·7H₂O), 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 certainty 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.
The potential of TCS systems effectively represents 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 to strengthen the efforts of the scientific community to have more and better alternatives for more energy-efficient technologies and to aim at the reduction of the impact of industries and other human activities upon the environment.

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 loses from other industrial or social activities – has been investigated from different angles. The capacity of engineered chemical systems has proven to be an approach for energy storage. This study has aimed to determine the current state of the investigations and technological advances of TES using lithium as part of the system.

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

- Scientific research on TCS systems based on chemical reactions are less abundant than sorption systems under the methodology applied.
- 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/H₂O and LiOH/H₂O 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.

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