The opportunities of lithium in thermal energy storage: A state-of-the-art review

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Abstract

Lithium, mainly used in electrical energy storage, has also been studied in thermal energy storage. It is recognized as a “critical material” and is produced from minerals and from brines. Chile is one of the biggest producers, here from brine and with lower costs than in other countries. With sensible heat storage, in solar power plants lithium is seen as a way to improve the properties of molten salts used today. The low melting point in these ternary salts with lithium, represent a considerable reduction in the maintenance and operational costs associated with current solar technology, demonstrating that the fluids showed, are potential candidates for TES in CSP plants. Many materials have been studied and proposed to be used as PCM. Between the multiple materials studied to be used in PCM, lithium materials and mixtures are listed as potential PCM for building applications and for high temperature applications. In thermochemical energy storage, lithium compounds have been used mainly in chemical heat pumps, following their use in absorption cooling.

Keywords: lithium; thermal energy storage; phase change materials; thermochemical energy storage; sensible heat

1. Introduction

Thermal energy storage (TES) is used to keep thermal energy to be used at a later time. A complete TES process involves at least three steps: charging, storing and discharging (Figure 1) [1]. The most important part of the storing step is the storage media. A wide variety of choices exists, depending on the temperature range and the application. For sensible heat storage, water is a common choice because, among its other positive attributes, it has one of the highest specific heats of any liquid at ambient temperatures. Solids have the advantage of higher specific heat capacities, which allow for more compact storage units. TES using latent heat change can also be used; the most common example of latent heat storage is the conversion of water to ice. The other category of storing heat it is considered through the use of reversible endothermic chemical reactions.

With the use of TES, systems achieve benefits by fulfilling one or more of the following purposes: increase the generation capacity, enable better operation of cogeneration plants, shift energy purchase to low cost periods, increase system reliability, or integrate other functions.

There are several types of TES methods, shown in Figure 2. Basically one can use a physical process or a chemical process. Physical processes are sensible heat storage and latent heat storage. Between chemical processes one can find sorption processes and chemical reactions.

Lithium is recognized as a “critical material”, that is, a material important to the clean energy economy and with risk of supply disruption [2] (Figure 3). Materials are deemed important or have a high impact based on the particular properties that make them well suited for applications in which they are used. For photovoltaics, this might be the semiconductor bandgap; for magnetic materials it might be the magnetic flux density; for thermal energy storage it might be the specific heat capacity or the phase change enthalpy. Lithium is always listed as a critical material in electric batteries [2,3]. Some of the materials are simply rare in their overall abundance in the earth’s crust, or do not commonly occur in single deposits with significant concentrations; others are difficult to recover economically; others are byproducts of primary production of other materials.

Lithium is produced mainly in Canada, Brazil, Australia, some areas of Africa and Russia as mineral, and in China, USA, Argentina and Chile from brines. 61.8% of the total world lithium resources come from brines, around 26.9 Mt [3-5]. The abundance in Earth’s crust is 19-21 ppm and in seawater 0.17-0.18 ppm [5]. The annual production in 2010 was 25,300 tons; its distribution and the reserves by country are shown in Table 1 [4]. When lithium ore is exploited, its typical grade is 0.57-0.3%, with a minimum economic ore grade of 0.2-1 % [5]. When comparing the productions costs of the lithium compounds from minerals and brines, countries producing lithium compounds from brines have lower production costs than those that produce them from minerals (2-3 $/kg vs. 6-8 $/kg) [6].

Chile is a country that has several advantages when producing lithium compounds from brines. On one side, in the North of Chile we can find the Atacama Salar that has higher lithium concentrations (0.15%) than other brines from lakes, and that has a composition of other elements (Mg, K, B) that favor high yields in the processes. On the other side, the area where the Atacama Salar is located has a climate that helps decreasing the production costs: high evaporation rates, high solar radiation, and low precipitation rates. All these facts indicate that Chile can produce lithium compounds at very low costs.

It is expected that in the near future Chile can go one step forward and to go from being a country exploiting lithium resources to become a country exporting products with lithium base that already exist in the market today (such as lithium batteries), and even developing new applications of lithium compounds, such as thermal energy storage materials by sensible heat (i.e. solar salt mixture with lithium additives), by latent heat (phase change materials base on lithium salt hydrates), and by thermochemical energy storage.

Lithium is mainly used in electrical energy storage, as the development of the electric car industry is based in lithium-ion batteries performance [4]. Lithium-ion batteries are also used for a wide range of electrical storage applications, from computers to video cameras. Lithium compounds are used in pharmaceuticals, as a mood stabilizer, and as an alloying agent to lighten and increase the strength of a number of metals, especially those used in the aerospace industry.

On the other hand, there are estimations of the lithium demand in the world, which give data on lithium demand by compound (Table 2) and by application (Table 3) [3]. It should be highlighted that meanwhile the demand of lithium compounds is expected to increase dramatically within the next few years, the application reviewed in this paper, thermal energy storage, is not even mentioned. Therefore, any deployment of lithium compounds for TES would need to be studied within this demand in other applications.

With known resources of lithium in the world of over 43 million tons, there is an abundance of physical lithium available to meet the demands estimated and shown above. The price of one kg of lithium metal is reported to be from 46 to 74.8 € [5].

The objective of this paper is to review the role that has played lithium compounds up to now in the different technologies of thermal energy storage, to evaluate the opportunities of lithium in them.

2. Sensible heat storage

The most common method for TES is sensible heat storage (Figure 4). Typical materials for sensible heat storage are solids such as stone and bricks, or liquids such as water. The amount of energy that can be stored in a sensible heat storage process can be calculated with:

$$\Delta Q = m \cdot c_p \cdot \Delta T$$

where ΔQ is the amount of energy stored, m is the mass of storage material involved, c_p is the heat capacity of the storage material, and ΔT is the temperature change occurred during the process.

For a proper performance, the materials used in a sensible heat storage system must meet some requirements. Physical requirements are having a large c_p (to allow adequate storage size) and a large thermal conductivity (to allow easy charging and discharging processes). Technical requirements can be summarized as having low vapour pressure, good chemical and physical stability and showing proper compatibility with container materials (no corrosion is required). Finally, economical requirements demand low price, non-toxic materials, and recyclability.

Typical materials used in sensible heat storage are rocks and buildings materials in building applications, water for domestic hot water, and ceramics and molten salts in high temperature applications such as solar power plants storage systems (Table 4).

The main applications of sensible heat storage are hot water production [1] and molten salts for solar power plants [7,8]. Lithium has been used to improve the properties of molten salts used today.

Figure 5 shows the lithium compositions studied in solar power plants thermal energy storage compared to the typical solar salt used commercially today. As it can be seen, the new compositions have nearly the same heat capacity (except for one), so the energy density of the system would be the same. In addition, the introduction of lithium nitrate is assumed to improve the performance of molten salts, extending temperature work range regarding with a low melting point as well as a higher thermal stability, which, in the short term, can be profitable despite the higher cost of operating plants with these fluids. The low melting point in these ternary salts with lithium (see Table 4), represent a considerable reduction in the maintenance and operational costs associated with current solar technology, demonstrating that the fluids showed, are potential candidates for TES in CSP plants.

There are very few estimations of the cost of energy stored, nevertheless the U.S. Department of Energy [9] presented the comparison between the today's commercially used solar salt (40% KNO_3 + 60% $NaNO_3$) with other candidates, between which several lithium compounds can be found (Table 5). The data shown demonstrate that although the cost of the salts when lithium is used increase considerably, the cost of a two tanks cost per stored energy would be much lower, due to the increase in energy density (Figure 6) and to the decrease of the cost of keeping the salts melted as mentioned before. It is important to point out the ternary mixture composed by 30% $LiNO_3$ + 60% KNO_3 + 10% $Ca(NO_3)_2$, shown in Figure 5. A synergetic effect between these additives could introduce interesting new formulations with lower final price. The search of new molten salts including these additives could be the key for novel TES materials with a higher energy density and a reasonable economic cost to take into account in the future application of new fluids for thermal energy storage and the further development of this technology.

3. Latent heat storage

Figure 4 presents a latent heat storage process, showing that in this case the storage happens while the phase change takes place, therefore it happens at constant temperature. Materials used in latent heat storage are usually referred to as phase change materials (PCM). The amount of energy stored is calculated with the following equation:

$$\Delta Q = m \cdot \Delta h$$

where ΔQ is the amount of energy stored, m is the mass of storage material involved, and Δh is phase change enthalpy. PCM can store about 3 to 4 times more heat per volume than is stored as sensible heat in solids or liquids in a ΔT of 20 ºC.

Latent heat storage presents an advantage to sensible heat storage when used in applications where stabilization of temperature is desired, such as buildings or transport boxes, or where heat or cold is stored with a small temperature change with high storage density, such as domestic water heating or storage in solar power plants with DSG systems.

Materials requirements can be also grouped in physical, technical and economical requirements. Again, the physical requirements will define the characteristics of the appropriate materials to be selected, but technical and economical ones should always be considered. These last two groups of requirements are the same to those listed in sensible heat storage, having to add small volume change in the technical ones. The physical requirements to PCM are having a suitable phase change temperature for the applications, having a large Δh and c_p, most of the times having also large thermal conductivity (in some applications this is not needed), and having reproducible phase change and little subcooling.

Many materials have been studied and proposed to be used as PCM. They are usually grouped by their nature: inorganic materials such as salt hydrates and salts, organic materials such as paraffin and fatty acids, and eutectics or other mixtures.

Although organic materials are non-corrosive, have low or non-subcooling and good chemical and thermal stability, their disadvantages push researchers to find appropriate inorganic materials. These disadvantages are a lower phase change enthalpy, low thermal conductivity, but mainly flammability (which is a big disadvantage in building applications) and low phase change temperature (which avoids their use in CSP systems) (Figure 7).

Between the multiple materials studied to be used in PCM, lithium materials and mixtures are listed as potential PCM for building applications (Figure 8) and for high temperature applications (see Figure 9) (Table 6).

Figure 8 shows the lithium compositions found in the literature to be used in building applications, together with two well-known PCMs, octadecane and Glauber salt. As it can be seen, the melting temperature of the lithium compositions is either around 10 ºC (useful for cooling), around 30-35 ºC, comparable to Glauber salt, and between 70 and 80 ºC (useful for domestic hot water). The heat of fusion is from 100 kJ/kg (considered the lowest to be commercially feasible) and 300 kJ/kg (considered a very high value for a salt).

When lithium compositions are used as PCM for high temperatures, one can compare their thermophysical properties to those of the solar salt, that has been studied also to be used as PCM. Figure 9 shows that the lithium compositions always have a higher heat of fusion, giving systems with higher energy density.

4. Thermochemical storage

Thermochemical energy storage happens when gas is absorbed in an absorbent, adsorbed in an adsorbent, or when there is a chemical reaction. Absorption happens with a gas being absorbed in a liquid absorbent; the heat involved is generally similar to the condensation heat of a gas, around 41 kJ/mol for water. Adsorption happens with a gas being adsorbed on a solid adsorbent; the heat involved is the condensation heat of a gas plus a light chemical bonding heat with solid surface, around 50-60 kJ/mol for a water system. Chemical reactions in thermochemical energy storage use the gas reaction with a solid reactant; the heat involved is the gas condensation heat, the light chemical bonding heat with the reactant surface, and the chemical reaction with the reactant, between 80 and 120 kJ/mol for a water system.

The main advantage of thermochemical materials (TCM) is that they present higher energy density than other storage methods (Figure 10). However, thermochemical energy storage also provides a wide range of operation temperatures and almost no heat losses during the storing period [24]. The main disadvantages of this technology are that it presents more difficulties to be implemented than the others, and that it is still in the research step. Nevertheless, a few lithium compositions have been studied to be used in chemical heat pumps.

Lithium compounds have been used mainly in chemical heat pumps. Chemical heat pumps are a representative of chemical thermal energy conversion and storage systems. A chemical heat pump is based on the reaction equilibrium relationship and has two operation modes. The operation cycle resembles the one of adsorption heat pumps used for cooling [25]. The chemical heat pump system operates in two successive phases (thermal conversion) or with a time gap (thermal storage mode): charging and discharging phase (Figure 11). The charging phase (regeneration, decomposition or desorption) occurs at high pressure (Ph). Heat at high temperature (Th) is supplied to the reactor and the solid (S’) decomposes. The gas (G) released from the decomposition is condensed by rejecting heat from the condenser at medium temperature (Tm). The discharging phase (reverse phase, production, synthesis or sorption) occurs at low pressure (Pl). The liquid evaporates by absorbing heat at low temperature (Tl) and the synthesis heat is released at Tm. In both phases the synthesis and decomposition occurs when the salt is removed from its equilibrium of temperature (equilibrium temperature drop, □T) and pressure (equilibrium pressure drop, □P) for heat and mass transfer [25]. The basic cycle shown in Figure 12 can be used to produce refrigeration at Tl and/or to produce heat at Tm.

Lithium has been used historically in chemical heat pumps, being used in one of the common pairs used in solar cooling applications, so in thermal conversion. Therefore, there are many studies that have developed lithium compositions to be used in chemical heat pumps for not only thermal conversion (in applications such as absorption cooling), but also thermal storage (Table 7).

5. Conclusions

Lithium is mainly used in electrical energy storage, as the development of the electric car industry is based in lithium-ion batteries performance, it is recognized as a “critical material” and, on the other hand, it is studied to be used in thermal energy storage in several applications. The main producer countries are Canada, Brazil, Australia, some areas of Africa and Russia as mineral, and China, USA, Argentina, and Chile from brines. But due to its specific characteristics, the production in Chile is cheaper than in other parts of the world.

Through sensible heat storage, in solar power plants lithium is seen as a way to improve the properties of molten salts used today. The low melting point in these ternary salts with lithium, represent a considerable reduction in the maintenance and operational costs associated with current solar technology, demonstrating that the fluids showed, are potential candidates for TES in CSP plants.

Many materials have been studied and proposed to be used as PCM: inorganic materials such as salt hydrates and salts, organic materials such as paraffin and fatty acids, and eutectics or other mixtures. Although organic materials are non-corrosive, have low or non-subcooling and good chemical and thermal stability, their disadvantages push researchers to find appropriate inorganic materials. These disadvantages are a lower phase change enthalpy, low thermal conductivity, but mainly flammability (which is a big disadvantage in building applications) and low phase change temperature. Between the multiple materials studied to be used in PCM, lithium materials and mixtures are listed as potential PCM for building applications and for high temperature applications.

In thermochemical energy storage, lithium compounds have been used mainly in chemical heat pumps, following their use in absorption cooling.

Acknowledgements

This work was partially funded by the Spanish project ENE2011-22722 and ENE2011-28269-C03-02. The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° PIRSES-GA-2013-610692 (INNOSTORAGE). Dr. Luisa F. Cabeza would like to acknowledge the Generalitat de Catalunya for the quality recognition 2009-SGR-534 and Dr. A. Inés Fernández for 2009-SGR-645. The authors acknowledge to FONDECYT (grant N° 1120422), FONDAP SERC-Chile (grant Nº 15110019), and the Education Ministry of Chile Grant PMI ANT 1201 for the financial support. Andrea Gutierrez would like to acknowledge to the Education Ministry of Chile her doctorate scholarship ANT 1106.

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Table 1. Reserves and production of lithium in 2010 [4].

Key producers 2010	Annual production* 2010		Reserves	Reserves/Production
	Tons	%	Tons	
Country				
Chile	8,800	35	7,500,000	852
Australia	8,500	33	580,000	68
China	4,500	18	3,500,000	778
Others	3,500	14	1,420,000	406
World	25,300	---	13,000,000	514
Company	2009			
Global Advanced Metals	4,300	25	n/a	n/a
FMC Corp	2,400	14	n/a	n/a
Potash Corp of Saskatchewan Inc	2,010	12	n/a	n/a

*Pure lithium metal

n/a – not available

Table 1. Lithium demand by compound (merchant market) – Forecast 2011-2025 [3].

Compound – MT LCE	2011	2015	2020	2025
Lithium carbonate	68,445	95,068	149,43	253,739
Lithium hydroxide	25,824	49,889	99,297	183,303
Lithium concentrate	19,229	25,683	31,393	36,757
Lithium metal	7,755	9,763	13,193	18,256
Butil-lithium	7,293	9,445	13,232	18,617
Lithium chloride	7,616	9,516	12,782	16,922
Other lithium compounds	3,893	5,368	8,103	12,525
Total demand	140,056	204,732	327,743	540,119

Table 2. Lithium consumption by application – Forecast 2011-2025 [2].

Application – MT LCE	2011	2015	2020	2025
Batteries – Portable devices secondary	27,416	44,865	71,009	105,236
Batteries – Portable devices primary	3,000	3,647	4,654	5,940
Batteries – HEV/EV	3,359	18,223	62,412	181,628
Batteries – 2WEVs	3,607	7,401	14,455	23,274
Batteries – Grid	500	2,500	5,000	7,500
Frits	20,000	24,308	30,581	36,320
Glass	17,000	20,662	25,993	30,872
Lubricating greases	18,000	24,249	34,641	44,211
Air conditioning	5,400	6,439	8,100	9,621
Continuous casting powders	6,000	7,154	9,000	10,689
Medical	4,000	4,502	5,194	5,876
Aluminum	5,000	5,933	7,464	8,865
Polymers	4,000	4,793	6,029	7,161
Others	12,000	14,308	18,000	21,379
Total Consumption	129,282	188,983	302,532	498,571

Table 3. Lithium compounds studied for sensible heat storage.

Storage Material	Type	Melting temp. (ºC)	Heat capacity (kJ/kg·K)	Melting enthalpy (kJ/kg)
KNO_3 + $NaNO_2$ + $LiNO_2$ + $NaNO_3$	Inorganic mixture	79 [9]	1.5048 [9]	n.a.
$LiNO_3$ + $NaNO_2$ + $NaNO_3$ + KNO_2 + KNO_3	Inorganic mixture	95.7 [9]	1.5455 [9]	n.a.
$LiNO_3$ + $NaNO_2$ + $NaNO_3$ + KNO_3	Inorganic mixture	99 [9]	1.5569 [9]	n.a.
KNO_3 + $LiNO_3$ + $NaNO_3$ + MgK+2KNO_3·$Mg(NO_3)_2$	Inorganic mixture	101 [9]	1.5788 [9]	n.a.
25.9% $LiNO_3$ + 20.06% $NaNO_3$ + 54.1% KNO_3	Inorganic eutectic	117 [9] 118 [10]	2.32 [9]	124 [10]
30% $LiNO_3$ + 18% $NaNO_3$ + 52% KNO_3	Inorganic mixture	120 [11]	n.a.	n.a.
20% $LiNO_3$ + 28% $NaNO_3$ + 52% KNO_3	Inorganic mixture	130.15 [12] 150 [11]	1.091 [12]	n.a.
30% $LiNO_3$ + 60% KNO_3 + 10% $Ca(NO_3)_2$	Inorganic mixture	132.15 [12]	1.395 [12]	n.a.
27% $LiNO_3$ + 33% $NaNO_3$ + 40% KNO_3	Inorganic mixture	160 [11]	n.a.	n.a.
$LiNO_3$-$NaNO_3$	Inorganic mixture	195 [11]	n.a.	252 [11]
12% $LiNO_3$ + 18% $NaNO_3$ + 70% KNO_3	Inorganic mixture	200 [11]	n.a.	n.a.
32.1% Li_2CO_3 + 33.4% Na_2CO_3 + 34.5% K_2CO_3	Inorganic eutectic	401 [13]	n.a.	221 [13]
80.5% LiF-19.5% CaF_2	Inorganic mixture	767 [7,14]	n.a.	790 [7,14]
LiF	Inorganic salts	850 [7,15]	1.64 [16]	682 [7,15]

n.a. – data not available

Table 4. Selected TES candidate salt mixtures with cost estimates [9].

Composition (wt. %)	Melting point (ºC)	Heat capacity (kJ/kg·K)	Energy density (MJ/m3)	Salt price (US$/kg)	Two tanks system cost / stored energy (US$/kWh$_{thermal}$)
40%KNO$_3$+60%NaNO$_3$	222	1.5381	756	1.080	31.21
KNO$_3$+LiNO$_3$+NaNO$_3$	117	2.32	1524	2.206	14.66
KNO$_3$+NaNO$_2$+NaNO$_3$	99	1.4623	1080	1.266	15.87
KNO$_3$+NaNO$_2$+LiNO$_2$ +NaNO$_3$	79	1.5048	1073	1.928	19.11
KNO$_3$+LiNO$_3$+NaNO$_3$ +MgK	101	1.5788	1181	1.537	16.15
LiNO$_3$+NaNO$_2$+NaNO3 +KNO3	99	1.5569	1114	1.809	18.27
LiNO$_3$+NaNO$_2$+NaNO$_3$ +KNO$_2$+KNO$_3$	95.7	1.5455	1110	1.797	18.23

Table 5. Lithium compounds studied for latent heat storage.

Storage Material	Type	Melting temp. (ºC)	Melting enthalpy (kJ/kg)
$LiClO_3 \cdot 3H_2O$	Inorganic (salt hydrate)	8 [1,17,19]	155 [15,17,18] 253 [1,17,19]
55%-65%$LiNO_3 \cdot 3H_2O$ +5-45%$Ni(NO_3)_2$	Inorganic mixture	24.2 [1,17]	230 [17,20]
$LiNO_3 \cdot 3H_2O$	Inorganic (salt hydrate)	30 [1,17-20]	189 [1,17-19] 296 [17,20]
$LiNO_3 \cdot 2H_2O$	Inorganic (salt hydrate)	30 [17,20]	296 [17,20]
$LiBr_2 \cdot 2H_2O$	Inorganic (salt hydrate)	34 [17,20]	124 [17,20]
$LiCH_3COO \cdot 2H_2O$	Inorganic (salt hydrate)	70 [17,20]	150 [17,20]
14% $LiNO_3$ + 86% $Mg(NO_3)_2 \cdot 6H_2O$	Inorganic eutectic	72 [17,20]	180 [17,20]
25% $LiNO_3$ + 65% NH_4NO_3 + 10% $NaNO_3$	Inorganic eutectic	80.5 [17,20]	113 [17,20]
26.4% $LiNO_3$ + 58.7% NH_4NO_3 + 14.9% KNO_3	Inorganic eutectic	81.5 [17,20]	116 [17,20]
27% $LiNO_3$ + 68% NH_4NO_3 + 5% NH_4Cl	Inorganic eutectic	81.6 [17,20]	108 [17,20]
$LiNO_3$ + $NaNO_3$	n.a.	195 [7,21]	252 [7,21]
$LiNO_3 \cdot 3H_2O$ + $LiNO_3$	Inorganic eutectic	301.4 [22]	264 [22]
$LiNO_3 \cdot 3H_2O$	Inorganic salt hydrate	303.3 [22]	287 [22]
43% Li_2CO_3 + 57% Na_2CO_3	Inorganic eutectic	500 [23]	348.5 [23]
80.5% LiF + 19.5% CaF_2	Inorganic eutectic	767 [7,14]	790 [7,14]
LiF	Inorganic salt	850 [7,15]	682 [7,15]

Table 6. Lithium compounds studied for chemical heat pumps.

Storage Material	Additive	Mass (kg)	Th/Tm/Tc	SCP (W/kg)	SHP (W/kg)	Time (min)	COP	Application	References
LiCl	EG (50%)	0.083	80/25/-5	117 W/kg of desorbing salt	---	30	0.47	Icemaker	[25,26]
LiCl/MgCl_2	Metal foam	1.8/1.8 (mass of the anhidrous salt)	200/155-200/20	---	222	40	0.11	Heat transformer	[25,27,28]
LiCl/MgCl_2	Metal foam	1.2/2.49 (mass of the anhidrous salt)	130/80-130/20	---	120	60	---	Heat transformer	[25,28,29]

Figure captions

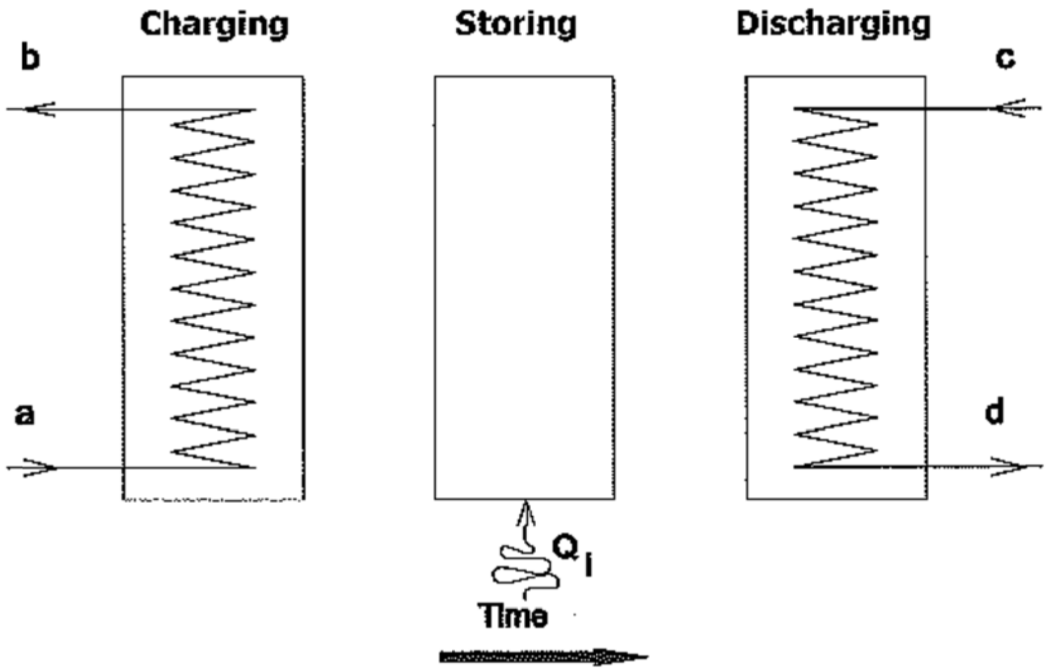

Figure 1. Steps in a thermal energy storage process [1].

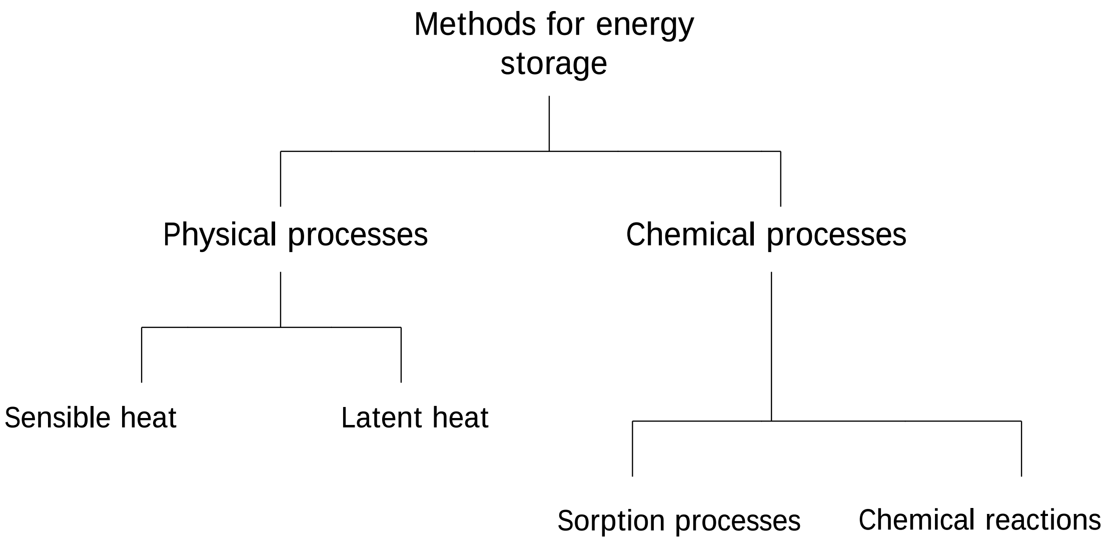

Figure 2. Methods for thermal energy storage

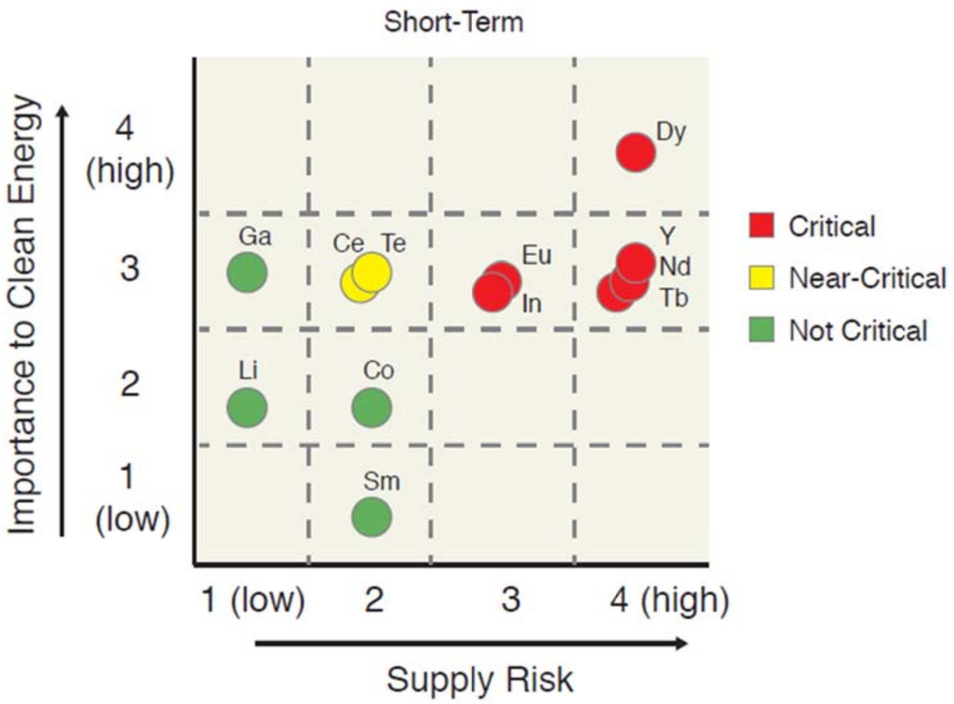

Figure 3. Critical materials matrix [2].

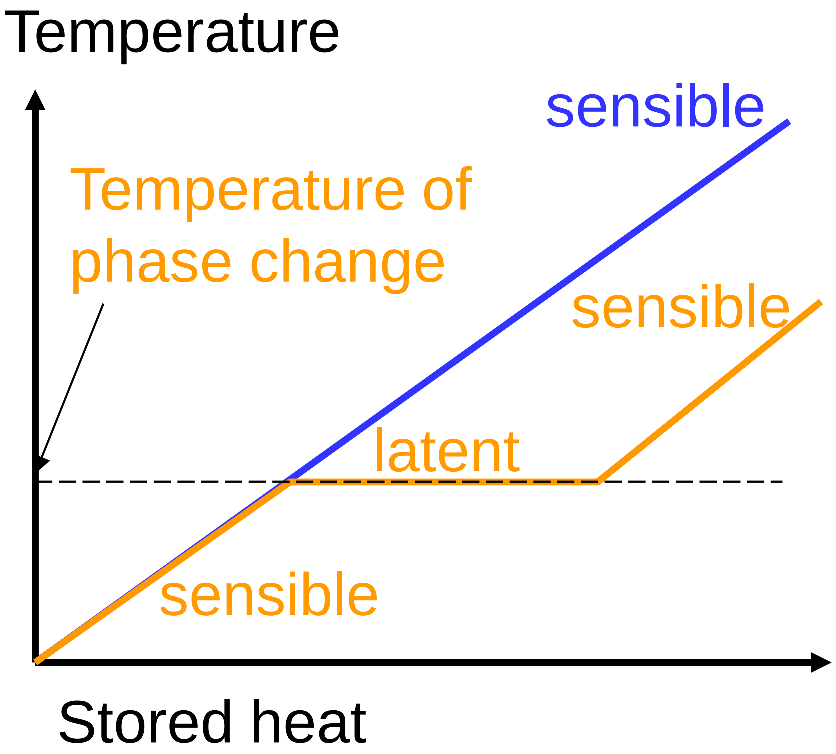

Figure 4. Sensible and latent heat storage processes [1].

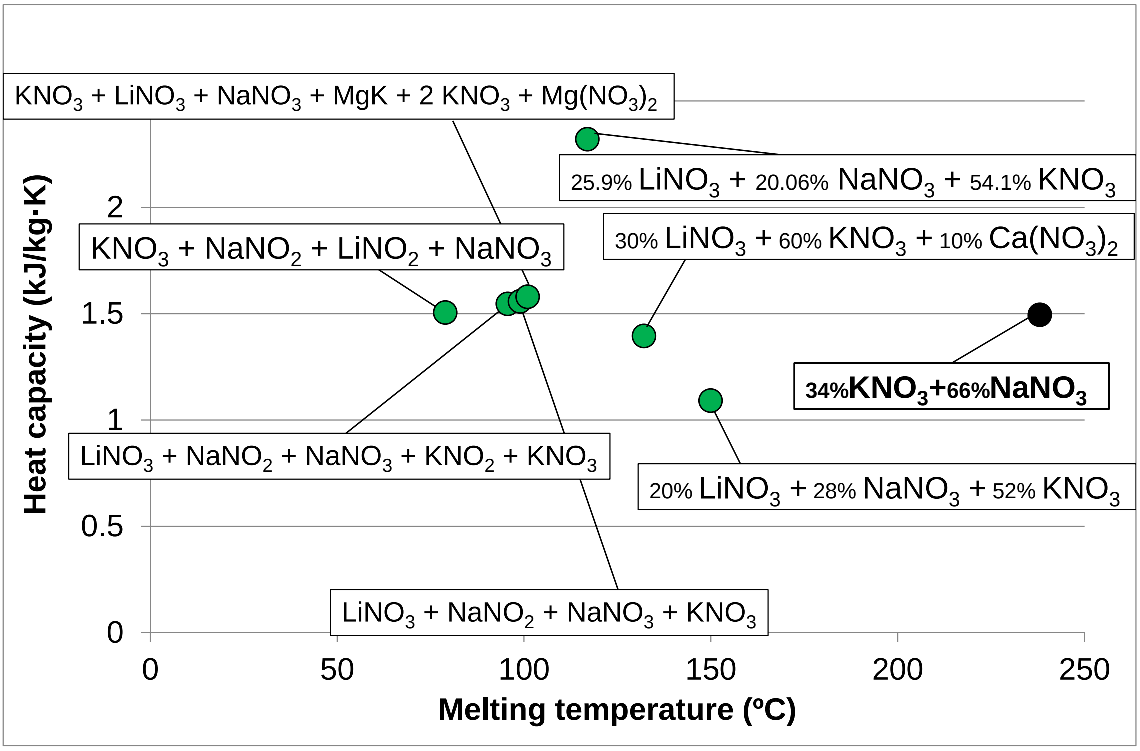

Figure 5. Heat capacity vs melting temperature of lithium compositions used in solar power plants TES systems compared to the commercial solar salt (wt%).

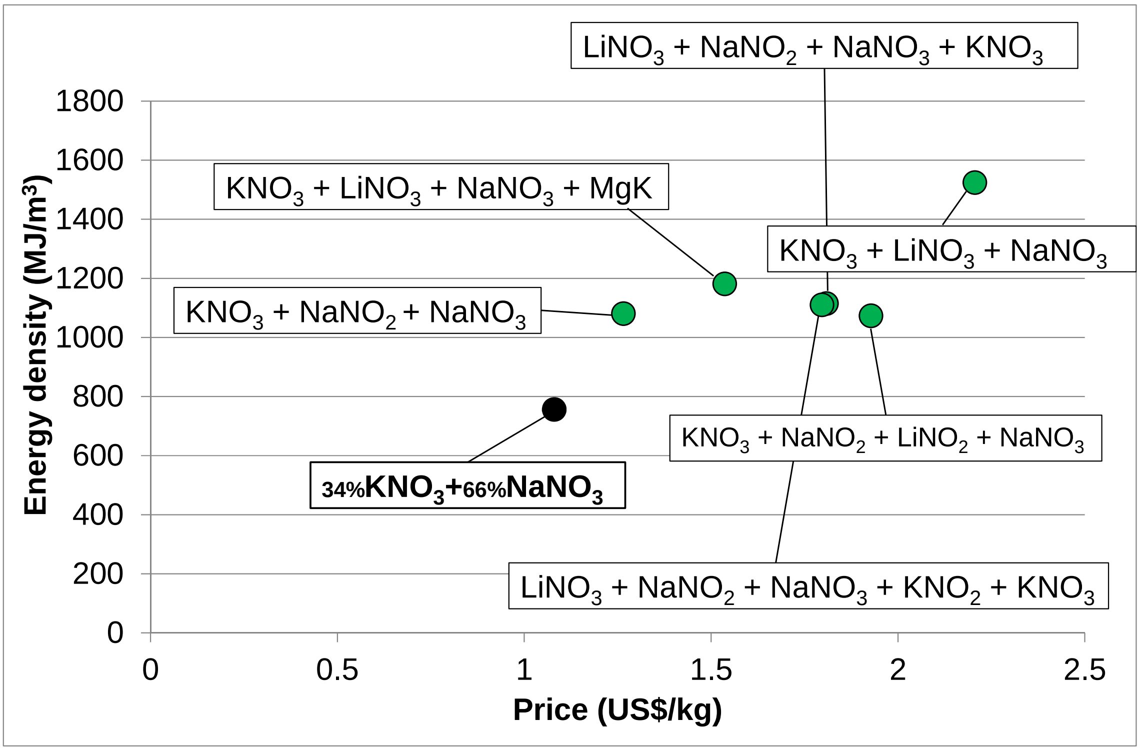

Figure 6. Energy density vs. Cost of Lithium compositions used as sensible TES systems compared to the commercial solar salt.

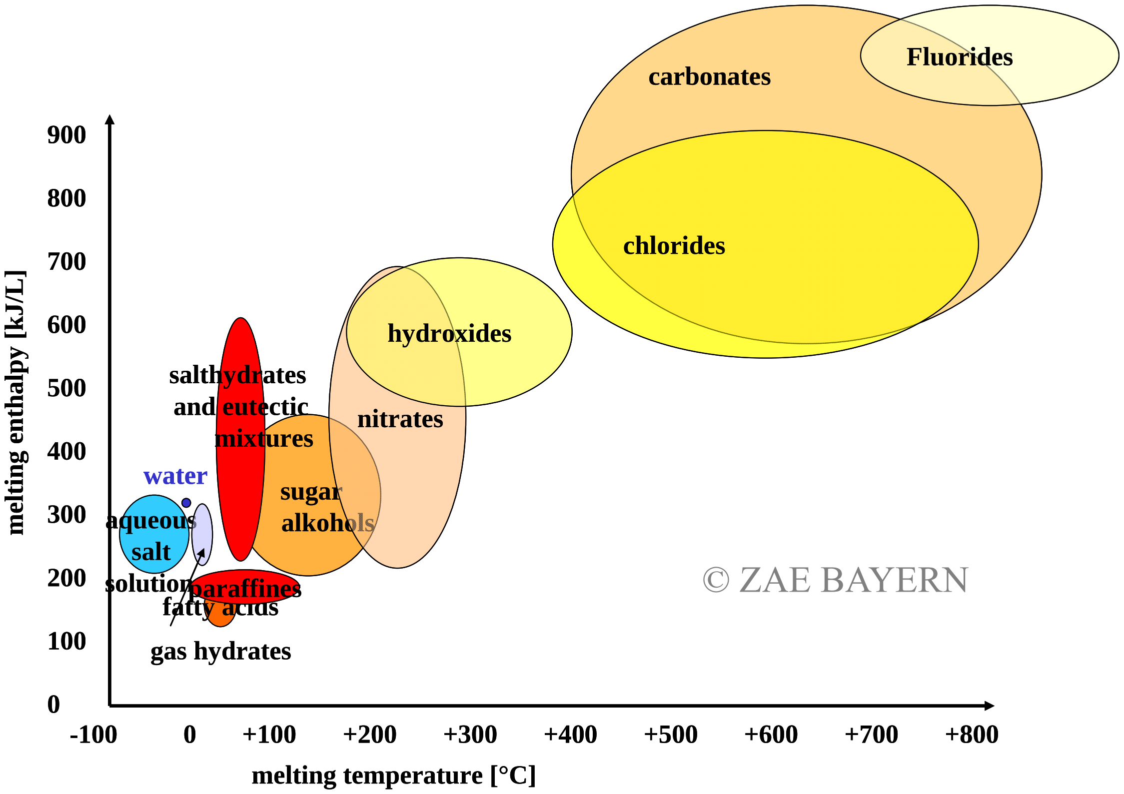

Figure 7. Types of materials used as PCM [1].

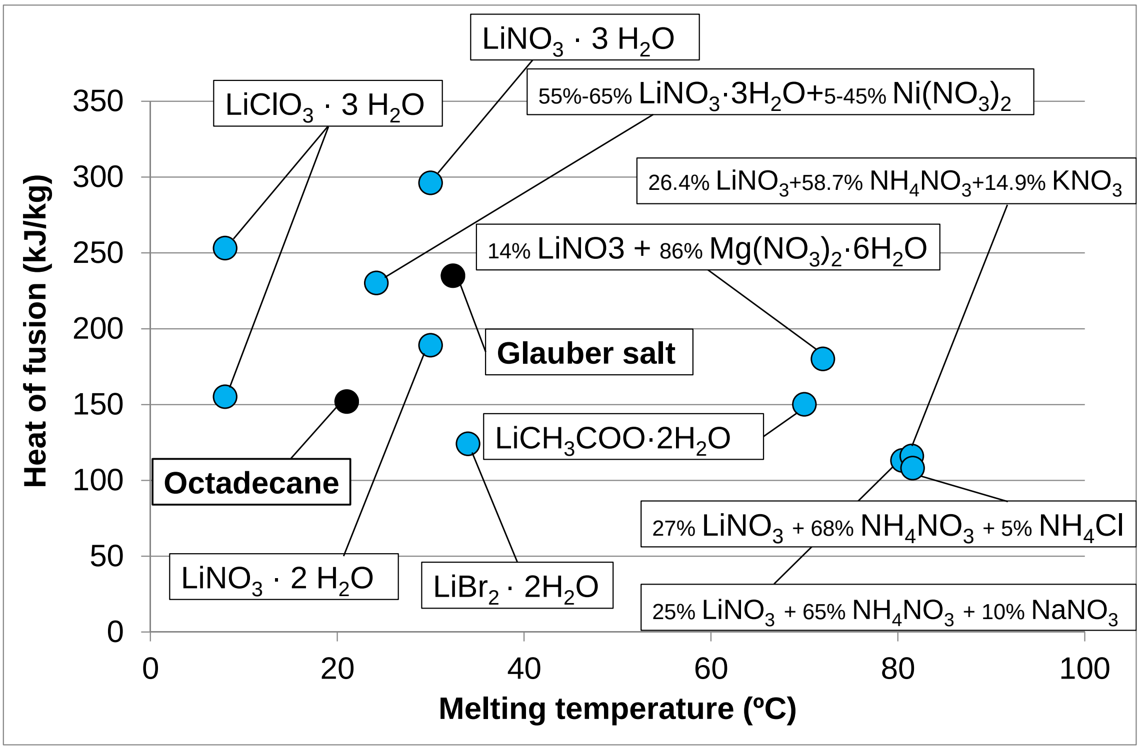

Figure 8. Lithium compositions used in building applications compared to the well-known octadecane and Glauber salt.

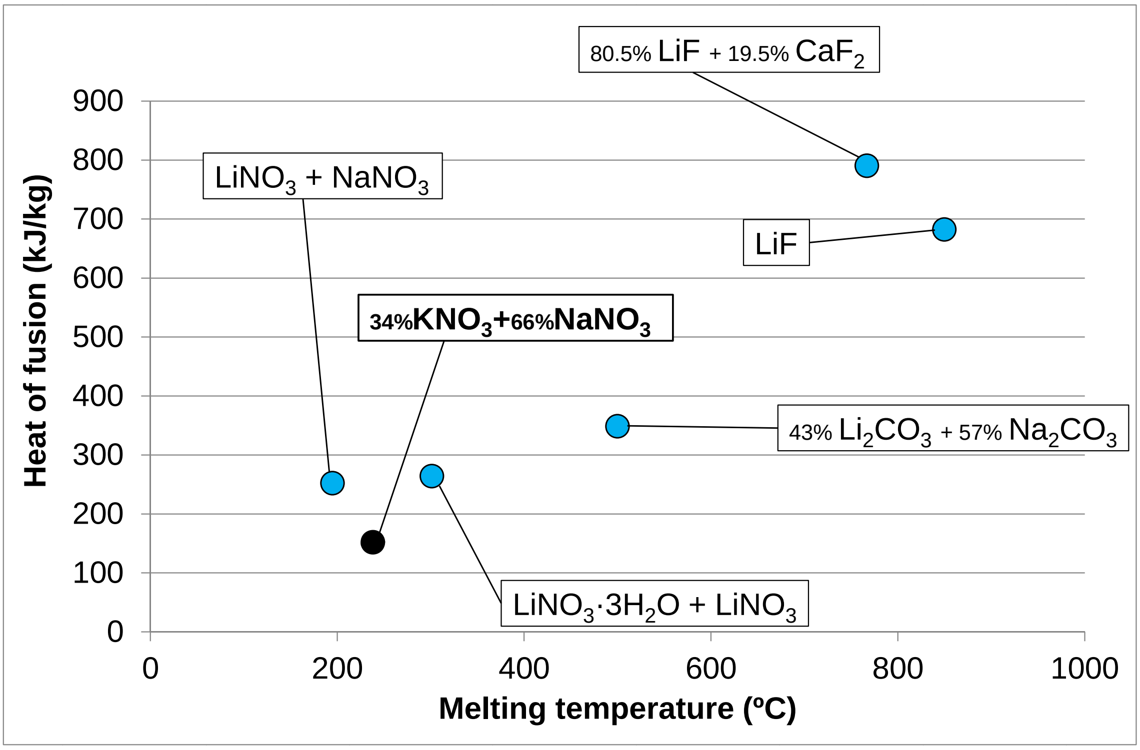

Figure 9. Lithium compositions used in solar cooling applications compared to the well-known solar salt.

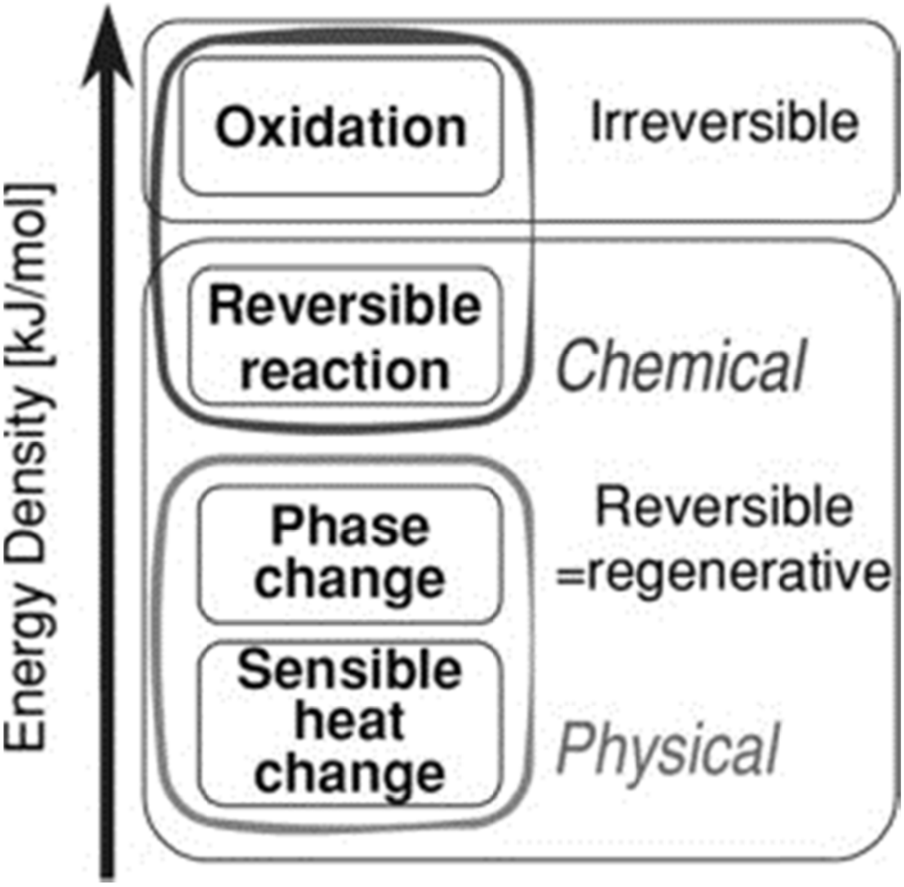

Figure 10. Energy density comparison between thermal energy storage methods [24].

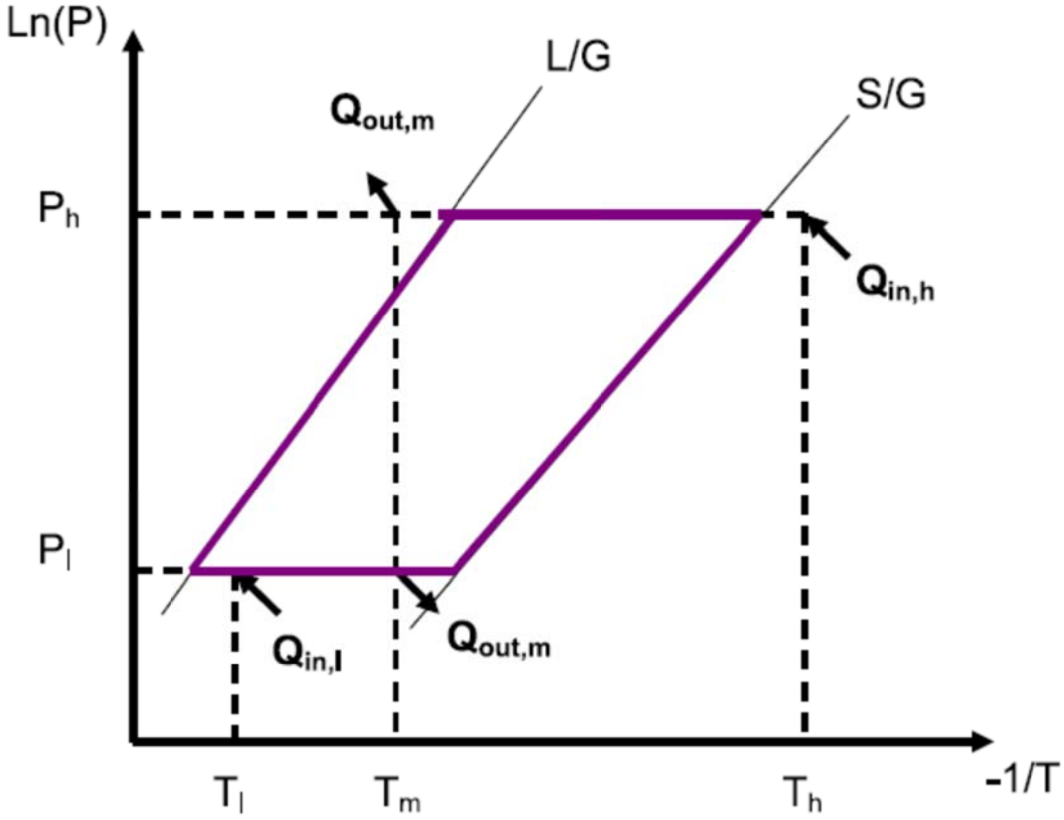

Figure 11. Working principle of a chemical heat pump [25].