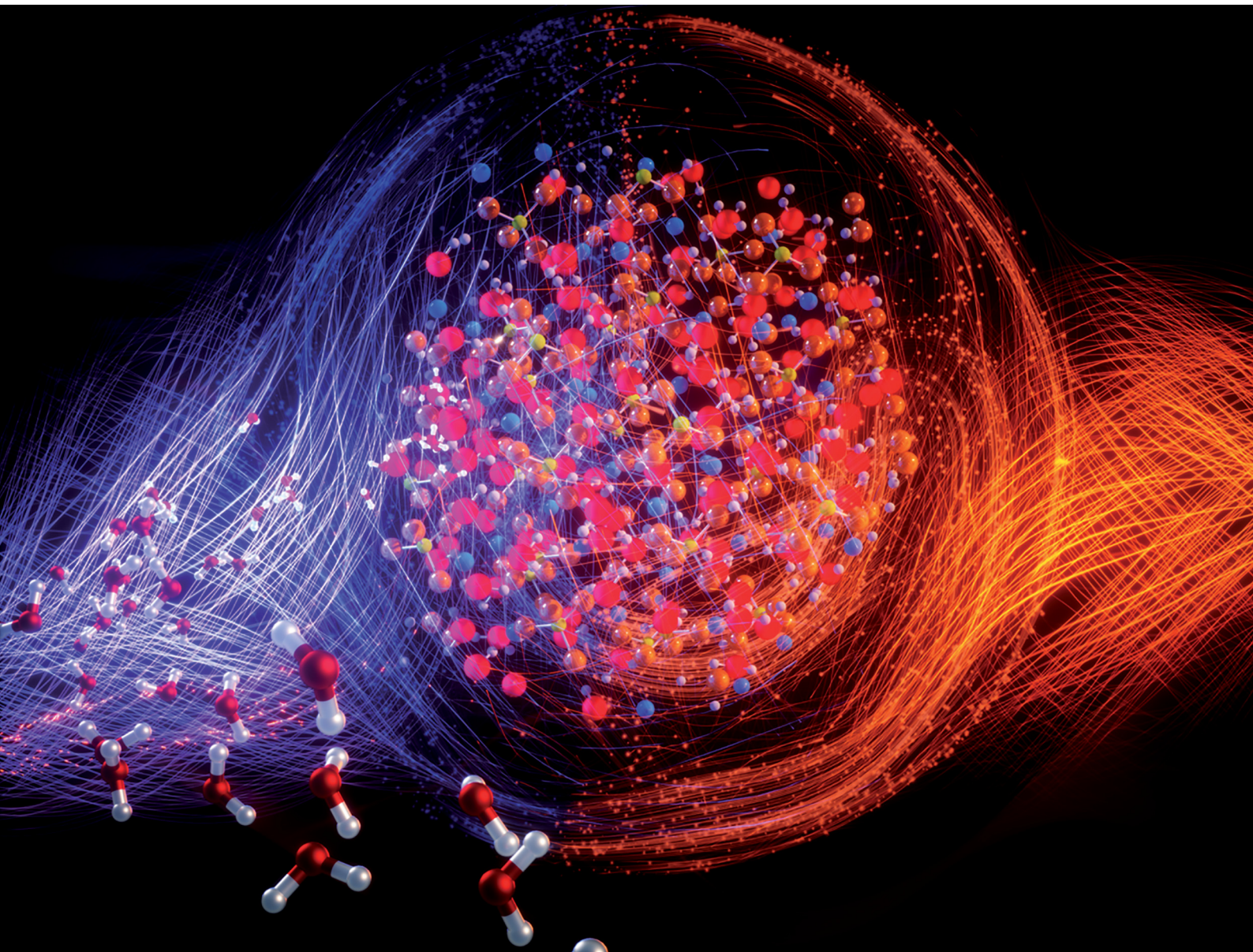


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conversion: attributes for low-temperature applications

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Materials for thermochemical energy storage and conversion: attributes for low-temperature applications

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The development of systems that can efficiently store and manage thermal energy – *i.e.*, heat – would improve the efficiencies of numerous processes throughout multiple sectors of the global economy. Nevertheless, the development of these thermal storage devices remains at a relatively early stage. To engage more researchers in the development of these devices and to accelerate their commercialization, this review presents an introduction to the properties of thermal storage materials that absorb and release heat through thermochemical reactions. Thermochemical materials typically exhibit the largest energy densities among all approaches to material-based heat storage. Nevertheless, they suffer from limited reaction rates and poor cycle life. An additional challenge is the multiscale nature of the energy storage process, which ranges from atomistic interactions that govern the storage of heat through alteration of chemical bonds, to mesoscale processes that control the transport of mass and heat. Following an overview of general concepts related to thermal energy storage, emphasis is placed on describing properties relevant for low-temperature applications. These applications include domestic heat storage/amplification (hot water heating), adsorptive cooling (air conditioning), and heat-moisture recuperation. Subsequently, detailed introductions are provided to the mechanisms and materials relevant for the three primary approaches to low-temperature thermochemical storage, including: (i) absorption in solids (hydrates, ammoniates, and methanlates); (ii) adsorption in porous hosts (zeolites, metal-organic frameworks); and (iii) dilution in liquids. For each category, advantages and shortcomings of benchmark and emerging materials are discussed. Finally, challenges and opportunities are highlighted for research aimed at developing optimal materials for thermochemical energy storage.

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Wider impact

Heat is a central component of the world's energy ecosystem. Examples of heat's prevalence include combustion engines, which convert heat into mechanical work, while heat from solar energy, geothermal wells, and the burning of fossil fuels is used to condition the air and water in homes, offices, and factories. In the U.S., approximately 10% of the energy consumed can be traced to residential heating and cooling alone. More generally, energy generation and use exhibit inefficiencies associated with large thermal losses – 66% of the energy produced in the U.S. in 2023 did no useful work and was lost to the environment as heat. Hence, technologies that capture, manage, and re-use heat have the potential to yield significant improvements in energy efficiency and expedite decarbonization. Thermal energy storage (TES) is one such technology. TES is predicted to reduce energy costs by 5–15% and peak electrical power demand by 13–33% globally. Despite these benefits, the development of TES systems remains in its infancy due to deficiencies in the underlying storage materials. This review introduces materials and mechanisms for low-temperature TES, emphasizing those that store heat using thermochemical reactions. Benefits, challenges, and high-priority research directions for thermochemical TES materials are described in detail.

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Introduction

Heat is a central component of the world's energy ecosystem. One example of heat's ubiquity is the production of heat in fossil-fuel-based combustion engines. The subsequent conversion of this heat into mechanical work is the basis for many of the transportation devices and industrial machinery that have been in use since the 19th century. In addition, heat from solar energy, geothermal wells, and combustion is used to condition the air and water in homes, offices, and factories.

Given its prevalence in our society, managing the flow and use of heat presents an opportunity for improving energy efficiency. For example, over two thirds of the energy produced in the United States – approximately 62 quadrillion BTUs – does no useful work, and is ultimately lost to the surroundings as heat.¹ This fraction of lost energy is typical of countries

worldwide.^{2,3} While the second law of thermodynamics limits the conversion of heat into work, the magnitude of these losses suggests that the capture, storage, and/or re-use of only a small fraction of this “lost” thermal energy would be beneficial. Furthermore, since the production of heat often occurs through the combustion of fossil fuels, strategies that maximize the use of the generated heat have the potential to reduce carbon emissions.

One technology for effective heat management is thermal energy storage (TES), *i.e.*, the storage of heat. Several studies have estimated the potential benefits of TES systems, and the results are promising. For example, in the European Union TES has been projected to achieve a 7.5% overall energy savings.⁴ Globally, TES is expected to reduce energy costs (by 5–15%) and peak electrical power demand (by 13–33%).⁵ TES is also one of the few technologies that can provide significant value in decarbonizing multiple use sectors.⁶ For example, TES has



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the projected potential to reduce carbon emissions by approximately 25% through the decarbonization of the energy grid.^{7,8}

TES has the potential to be applied in many contexts and for multiple applications:

Buildings

Applications of TES in buildings can improve the performance of heating, ventilation, and air conditioning (HVAC) systems.^{9–11} Approximately 21% of the energy consumed in the U.S. can be traced to residential applications,¹² 48% of which is devoted to heating and cooling.¹³ Because approximately 75% of all waste heat generated is below 100 °C (a temperature suitable for use in buildings), there is a high reuse potential for this lower-temperature heat in domestic heating applications. Improvements to HVAC made possible by TES will translate to higher efficiencies, lower operating costs, and reduced CO₂ emissions through reduced consumption of the fossil fuels used to generate the electricity that powers HVAC devices.

Preservation of perishables

TES systems offer an increase in thermal inertia, which is measured by the responsiveness of a system's temperature to the supply or withdrawal of heat. As thermal inertia increases, a greater amount of heat is required to change the system's temperature. This feature of thermal energy storage systems has been exploited to preserve food and other perishables by maintaining them at low temperatures. A common example is the use of ice as a phase-change material, but containers with even greater thermal inertia have been developed. For example, the Greenbox Thermal Management System has been used to keep vaccines and other temperature-sensitive medical supplies cool during long periods of transportation.¹⁴

Electronics

TES can be deployed to protect sensitive electronics.^{15,16} As electricity flows through a circuit, the resistance of the circuit results in

energy loss through heat. This heat can physically damage fragile components in a circuit. As such, either cooling or a heat sink (a TES system) can aid in maintaining acceptable temperatures.

Vehicles

TES can be used in vehicles to condition the temperature of engines.^{17–19} When a vehicle starts from cold conditions, several minutes of operation are needed before a steady operating temperature is achieved. When cold, the engine operates less efficiently, consumes more fuel, and the exhaust gases from the engine are lower in temperature, resulting in a less effective catalytic converter. A TES system can aid in preheating the engine by capturing waste heat from prior operation, thereby reducing the inefficiencies associated with cold start. Further benefits can be derived by using TES as a thermal sink to reduce overheating under high tractive efforts.²⁰

Thermal batteries

A thermal battery, *i.e.* a system that captures and stores heat for later use, is a generalization of the cold-start TES application discussed above. Thermal batteries have been proposed to capture waste heat from industrial processes, operating in the range of 100–300 °C.^{21–24} This captured heat is then used for electricity production, thus increasing the overall efficiency of the cogeneration scheme. TES can also be used in conjunction with solar energy generation.^{25,26} The availability of solar energy fluctuates due to weather conditions and according to daily and seasonal cycles. By storing excess solar energy, a TES-enabled solar plant can provide output that is less dependent on the instantaneous solar conditions to meet time-varying energy demand.

The examples mentioned above illustrate that TES systems can take a variety of forms. Nevertheless, at their core all these systems share the common trait of employing a material that stores thermal energy. These materials store heat in one of three ways: as sensible heat, as latent heat, or as thermochemical heat.



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Sensible heat storage

All materials store sensible heat within the kinetic energy of atomic vibrations. The amount of heat stored is indicated macroscopically by the temperature. Materials with higher specific heat capacities store more sensible heat for a given temperature increase; therefore, these materials tend to store heat with higher energy densities. Liquid water, with its high specific heat capacity, is a common medium for sensible heat storage. Other materials such as alcohols, plastics, concrete, molten salts, and metals have also seen use in sensible heat storage systems.⁹

Sensible heat storage is the simplest form of TES. It has the advantage of being reversible, so long as changes to the operating temperature – which can trigger phase transformations – are avoided. However, sensible heat storage is characterized by low energy densities (Fig. 1). Thus, it is not suitable for applications where lightweight and/or compact TES systems are required. Furthermore, sensible heat storing materials will lose stored energy if the system is not well insulated. This limits its use in applications that target long-duration storage.

Latent heat storage

Another method of TES exploits the latent heat of a phase transformation. To implement this approach, the so-called phase change materials (PCMs) are used.^{9,27} A common example is an ice cube that keeps a drink cool. Here, heat transferred from the surroundings is absorbed by the ice as the

(endothermic) latent heat of melting. These phase changes occur at a specific temperature, which dictates the temperature at which the material will store or release heat. PCMs have 2–6 times greater energy densities than sensible heat-storing materials.²⁸ However, the change in the material during phase change can lead to practical issues, such as melting/solidification temperature hysteresis and volume change.

Thermochemical energy storage

Lastly, thermochemical materials store heat by undergoing a reversible chemical reaction or sorption process. A typical thermochemical energy storage (TCES) reaction takes the form:



In the forward endothermic reaction, material *A* decomposes into material *B* and working fluid *C* while simultaneously absorbing heat *Q*. Unlike PCMs and sensible heat storing materials, thermochemical heat storing materials do not discharge energy over time as the energy is stored in the form of the chemical potential of the products, as long as they remain physically separated. When *B* and *C* are recombined and react, the reverse exothermic reaction occurs, re-forming *A* and releasing the stored heat. In the case of a sorption-based thermochemical process, *B* represents the sorbent, *C* is the sorbate, and *A* is the sorbate-sorbent complex. TCES materials have the largest energy densities of all TES materials, reflecting the large amount of energy that can be stored by a chemical reaction. However, the chemical reaction also poses some complexities. For example, it is common for these materials to experience irreversibility due to side reactions as well as slow kinetics due to limitations in mass and/or heat transfer.^{29,30}

Fig. 1 shows a “temperature ladder” for various TES materials,^{31–40} as well as temperature ranges^{9,17,21,31,41} for various TES applications. Although they exhibit more practical complexity, thermochemical heat storage materials offer significantly higher energy densities on the material level. Additionally, the temperature ladder shows a general correlation between the operating temperature of TES materials and their energy densities. One reason for this is that higher enthalpies of transformation, ΔH , associated with the relevant chemical reaction or phase change, correlate both with higher thermodynamic equilibrium temperatures and energy densities. This correlation is useful for understanding the limits of energy density for a particular application, as materials are generally chosen based on the target operating temperature. In some cases, it is possible to use all three methods in one material, thus boosting energy storage density.⁴²

Although Li-ion batteries have experienced significant cost reductions, the low efficiency of converting heat to electricity suggests that batteries are less efficient options for energy storage when the energy to be stored is in the form of heat. For example, modern thermoelectric devices convert heat to electricity with efficiencies in the range of 5 to 15%.^{43,44}

The preceding discussion illustrates that the field of TES is broad, encompassing many different applications, materials, and system designs. The present review provides an overview of

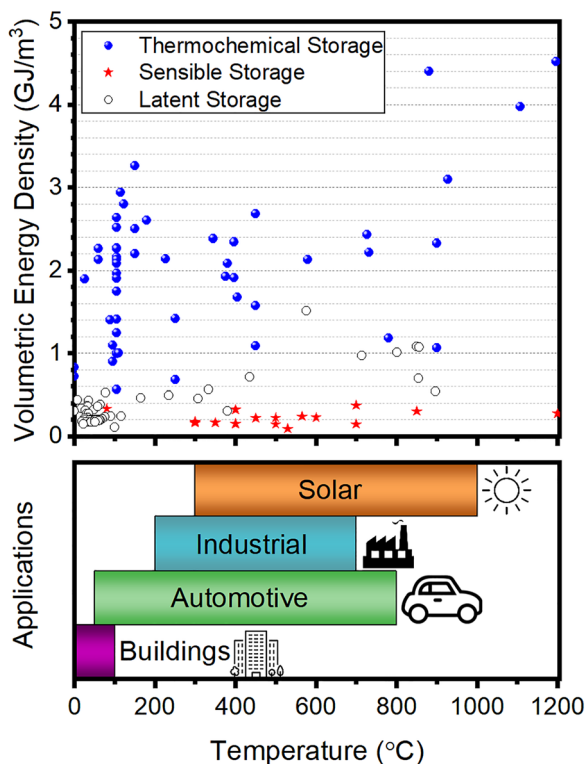


Fig. 1 Temperature ladder for thermal energy storage materials and their typical storage densities (top). The general temperature ranges for various thermal energy storage applications are also shown (bottom).



an important subset of the field, specifically focusing on thermochemical and sorptive heat storage materials that operate at low temperatures (*i.e.*, below ~ 100 °C). Additionally, applications that operate in the low temperature region of interest, including TCES systems in buildings, are briefly discussed to illustrate the implications for material selection and characterization. The materials of interest include salt hydrates, porous media, and liquid absorption of gases. Key properties of these materials are discussed, including thermodynamic operating conditions, energy density, kinetic performance, stability, and several non-technical aspects. The review concludes with a discussion of current challenges and opportunities in the field.

Materials performance criteria and example applications

A. Criteria for materials selection

Several performance criteria exist for TCES systems (Fig. 2). These criteria can be loosely divided into those based on thermodynamic, dynamic, and ‘other’ characteristics. Thermodynamic criteria refer to the capacity and efficiency with which heat is stored (*e.g.*, COP, second-law efficiency). Dynamic criteria refer to the rate at which thermal energy is stored or released (power and cycle time). Other important characteristics include safety, cost, and energy density.

Since the properties of the TCES material strongly influence the performance of the resultant TCES system, the system

criteria illustrated in Fig. 2 can also be used to guide material selection. Additional application-specific requirements (*e.g.* low toxicity for domestic usage) or system design constraints (open/closed, fixed or moving bed) should also be accounted for when selecting suitable TCES materials.^{45–48} This selection task is further complicated by the presence of design trade-offs (*e.g.* storage density *vs.* temperature lift^{49,50}) and limited understanding of the relative importance of the various materials attributes in determining system performance.

Table 1 summarizes performance targets associated with several key properties of thermochemical energy storage systems and materials, as proposed by the U.S. Department of Energy (DOE) and the European Technology and Innovation Platform on Renewable Heating and Cooling (RHC-ETIP).^{51,52} The target for energy density at the system level, 200 and 220 kWh m⁻³, respectively, is similar for both the DOE and RHC-ETIP. Translating this system-level target to an energy density at the material level requires knowledge of the volume occupied by the non-active components of the storage device. These components will vary depending on the system design (open *vs.* closed), and may include heat exchangers, evaporators, storage vessels, *etc.* Hence, to account for the volumes of the non-active components, a target for the energy density of the storage material should exceed that for the system. N'Tsoukpoe compared the system-level and materials-level energy densities of several prototype thermal storage systems.⁵³ Their analysis found that in most cases the system-level energy densities were significantly smaller than that of the active material. In the best cases, the system energy density was 30% to 50% of the materials-only value. Assuming that these (best case) systems represent what can be achieved through system design optimizations, then a reasonable target for the materials-level energy density would be two to three times the system-level target, or 400–600 kWh m⁻³.

Below, important materials selection criteria are described for applications including domestic heating, cooling, heat-moisture recuperation in buildings, and water harvesting.

Thermodynamic criteria. The thermodynamic properties of a TCES system refer to the amount and quality of thermal energy processed.

First-law efficiency. The first-law efficiency or the Coefficient of Performance (COP) of a TCES system is defined as follows:

$$\text{COP} = \frac{|Q_{\text{useful}}|}{Q_{\text{input}}}, \quad (2)$$

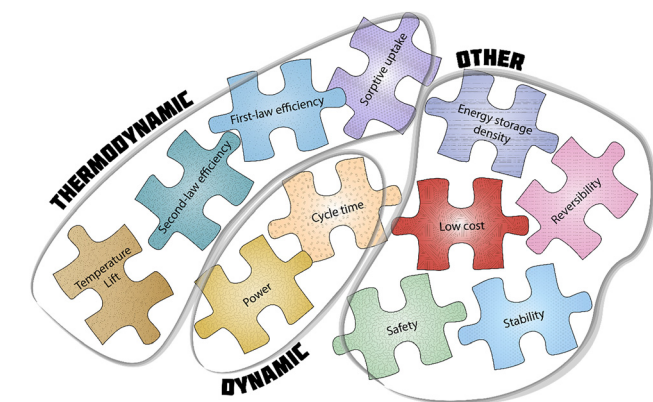


Fig. 2 Examples of thermodynamic, dynamic, and other selection criteria relevant for thermochemical heat storage systems.

Table 1 Performance targets for domestic thermochemical energy storage

| Property | Target | Comments |
|------------------------------------|--|--|
| System-level energy density | 200 kWh m ⁻³ ⁴⁹ 220 kWh m ⁻³ ⁵² | Based on U.S. DOE and RHC-ETIP |
| Materials-level energy density | 400–600 kWh m ⁻³ | Assumes system energy density is 30%–50% of materials energy density ⁵³ |
| Cost of composite storage material | < \$15 per kWh ⁴⁹ | Includes active material and materials that facilitate heat/mass transport |
| Thermal conductivity | > 1.0 W m ⁻¹ K ⁻¹ ⁴⁹ | For composite storage material |
| Capacity retention and cycle life | > 90%, 7500 cycles or 20 years ⁴⁹ 25 years ⁵² | |
| Subcooling/supercooling | < 2 °C ⁴⁹ | Low temperature hysteresis desired for charging/discharging |



where Q_{useful} is the amount (or flow) of useful heat from a system, and Q_{input} is the total amount (or flow) of heat that drives a cycle under consideration. For thermal energy storage, a larger COP implies that a greater amount of useful heat can be recovered upon discharging relative to the lower-grade heat supplied to the system upon charging. A high COP can be achieved by minimizing thermal losses incurred during charging or discharging, for example by minimizing hysteresis and improving the system's kinetics. For water as the working fluid, the COP for TCES systems is usually less than 1.^{54,55} For thermally-driven TCES applications where the input energy Q_{input} is available "for free" from, for instance, a solar concentrator or a PV panel, the COP is often not a highly-relevant quantity.

Temperature lift. Temperature lift, TL_{eq} , is another parameter that is meaningful for heat storage systems. Thermodynamic temperature lift may be defined as:

$$TL_{\text{eq}} = T_{\text{release}}(\text{eq}) - T_0 \quad (3)$$

Here, $T_{\text{release}}(\text{eq})$ is the equilibrium temperature for the heat release process and T_0 is the ambient temperature, which is equal to the temperature of the working fluid.

Second-law efficiency. The second-law efficiency (or exergy efficiency) describes the usefulness of the heat recovered upon charging and discharging a TCES system.⁵⁶ The exergy, A , of a heat transfer process is defined in terms of the Carnot factor as:

$$A = \left(1 - \frac{T_0}{T}\right)Q, \quad (4)$$

where T_0 is the ambient temperature, T is the temperature at which heat is transferred, and Q is the amount of heat transferred. By analogy with eqn (2), one can introduce the exergy efficiency, Ψ , of a system:

$$\Psi = \frac{|A_{\text{useful}}|}{A_{\text{input}}}$$

where A_{useful} is the amount (or flow) of useful exergy from a system, and A_{input} is the total input amount (or flow) of exergy. Exergy quantifies the usefulness of heat by quantifying how much work could be extracted from 1 J of heat supplied to an ideal machine operating with Carnot efficiency. For instance, a material releasing "useful" heat at 299 K with $T_0 = 298$ K will not be suitable for TCES as the number of "useful" Joules (exergy) extracted will be low, even if Q_{useful} is large. For a similar reason, low values of temperature lift for TCES systems yield low values of exergy efficiency. For many solid-state transformations, a substantial metastability is observed (discussed below), which results in sluggish kinetics for heat storage and/or release close to equilibrium.⁵⁷ Such metastability lowers the exergy efficiency, thus limiting the material's applicability for TCES. However, we note that despite low exergy efficiency for some TCES cycles they still may be appropriate for certain low-temperature applications where heat is used directly, e.g. space heating or drying.

Dynamic criteria. Heat must be absorbed or released at sufficient rates for a TCES system to be practically useful.

Heating power. Heating power, W , is the most straightforward way to quantify the rate of heat or cold storage/release:

$$W = \frac{dQ_{\text{useful}}}{dt} \quad (6)$$

The heating power is predominantly determined by the system design and by material properties such as the rate of heat/mass transfer within the material bed. For a bed of TCES particles, thermal conductivity, heat capacity, and the diffusion coefficient are important factors in achieving an optimal bed design.⁴⁸

Cooling power or SCP. Cooling power or specific cooling power, SCP, is defined as the amount of heat absorbed by a system per unit time divided by either the mass of the material (m):

$$SCP = -\frac{1}{m} \frac{dQ_{\text{useful}}}{dt} \quad (7)$$

or by its volume (V):

$$SCP = -\frac{1}{V} \frac{dQ_{\text{useful}}}{dt} \quad (8)$$

Cycle time. Cycle time is another important factor that affects material selection. For short-term cycles (e.g. daily storage) adsorption on a surface or absorption in a liquid is often preferable for TCES. On the other hand, for long-term storage, chemical reactions involving absorption in solid materials are preferred due to their lower tendency for heat losses.

Dynamic temperature lift. An alternative form of temperature lift, termed dynamic temperature lift, TL_{dyn} , is commonly used in studies dedicated to TCES prototypes. In this case the temperature lift is defined as the temperature reached during discharging, T_{release} , at the outlet (maximal or average) minus the initial temperature, T_{inlet} , of the heat transfer fluid (HTF):⁵⁸

$$TL_{\text{dyn}} = \max(T_{\text{release}}) - T_{\text{inlet}} \quad (9)$$

Other criteria. Other aspects of TCES materials relevant for domestic applications include:

- Energy storage density (ESD, energy stored per unit volume of the material, bed, or the device) and specific energy (energy stored per unit mass)
- Amount of working fluid (or sorbate) exchanged during the cycle Δw , g g⁻¹ (for cooling, moisture recuperation, water harvesting)
- Presence/absence of side reactions (i.e., chemical degradation)
- Reversibility of reaction or sorption/desorption
- Mechanical properties (compressibility, volume change, flowability – for moving beds)
- Cost (per unit of processed energy)
- Toxicity (high LD₅₀, mg kg⁻¹)
- Flammability



The above criteria point to challenges associated with the use of several materials for domestic applications, for instance, those based on ammonia or methanol (due to toxicity and flammability) or those involving compounds of expensive metals.^{39,45–47,59} While the costs of new technologies that rely on the sourcing of materials that are not in wide use can initially be high (such as for the TCES systems discussed here), rapid cost reductions have been demonstrated in related technologies by exploiting economies of scale. For example, the cost of Li-ion batteries has decreased by approximately 97% over the past three decades.⁶⁰ We anticipate that similar cost reductions can be achieved for the materials relevant for TCES.

B. Example applications for TCES

Domestic heat storage. A thermochemical energy storage system for domestic applications may be considered a thermally-driven heat pump based on endothermic decomposition (or desorption) and exothermic synthesis (or sorption) reactions.⁴⁷ Fig. 3 shows an ideal thermodynamic cycle of a domestic TCES system, which consists of two isobars and two isosteres. During storage or charging (process 3 → 4) the material is decomposed at $(T_{\text{storage}}, P_{\text{dec}})$ while the resultant gas is condensed at T_{cond} in the condenser (or ejected to the surroundings for an open system). Once the decomposition is complete (4), the heat is stored in the form of chemical potential which is constant across isosteres (2–3 and 1–4 in Fig. 3). In a domestic storage cycle, heat is released at $T_{\text{release}} < T_{\text{storage}}$ during synthesis by evaporating the working fluid at $(P_{\text{syn}}, T_{\text{evap}})$ while bringing it in contact with the charged thermochemical material. The cooling effect in the evaporator is produced simultaneously with useful heating.

The most popular closed TCES systems exchange only heat with the surroundings. These consist of an adsorber–desorber for decomposition/synthesis of the TCES materials and an evaporator–condenser for the evaporation/condensation of a working fluid. In contrast, open systems exchange the working fluid with the environment and do not require a separate vessel for condensation.

For both open and closed systems the adsorber–desorber subsystem often consists of a packed bed of an active storage

material with an integrated heat exchanger.⁶¹ Alternatively, one can decouple decomposition–synthesis and storage by allowing them to occur separately in a heat exchanger and a storage tank, respectively. However, this approach requires the transport of the storage material from the storage vessel to the heat exchanger; such systems are referred to as moving bed systems. Each system design has advantages and drawbacks; helpful reviews of these topics can be found elsewhere.^{30,62}

For domestic heat storage, the boundary temperatures and pressures are defined by the available source(s) of heat to be stored and by the heating demand. Ideally, decomposition would be driven by a solar collector/PV panel with typical temperatures $T_{\text{storage}} = 80\text{--}100\text{ }^{\circ}\text{C}$, while the condensation of the working fluid (water) would occur at near ambient temperature, $T_{\text{cond}} = 25\text{--}30\text{ }^{\circ}\text{C}$.⁴⁷ The stored heat may be used for space heating ($T_{\text{release}} = 30\text{--}45\text{ }^{\circ}\text{C}$) or for the production of hot water ($T_{\text{release}} = 60\text{--}70\text{ }^{\circ}\text{C}$) by upgrading low-temperature heat taken from the environment (*e.g.* from geothermal wells or directly from air) at $T_{\text{evap}} = 5\text{--}25\text{ }^{\circ}\text{C}$. While these boundary conditions are typical for domestic applications (Table 2), more exotic examples include decomposition *via* an electric heater at $T_{\text{storage}} > 300\text{ }^{\circ}\text{C}$ ⁶³ or upgrading heat using a temperature difference between air ($-40\text{--}25\text{ }^{\circ}\text{C}$) and water ($2\text{--}3\text{ }^{\circ}\text{C}$) in colder climates for space heating.⁶⁴ In the latter case, the so-called “heat-from-cold” (HeCol) cycle differs from the one presented in Fig. 3 as the sorbent is regenerated *via* pressure rather than through a temperature difference.^{65,66}

The criteria for material selection in domestic heating applications arise from space constraints for the TCES system, and from temperature requirements for hot tap water or space heating. Consequently, energy storage density (*i.e.* the amount of heat stored per cubic meter of the storage bed or device), temperature lift, power, and cyclability are the most relevant parameters. Material toxicity is also a concern as many governments impose restrictions on working fluids for refrigerants used in the domestic environment (*e.g.* ammonia or methanol). Unsurprisingly, material price per unit of stored energy is also an important criterion.⁶⁷ Additional system-specific requirements on the storage materials may be introduced – *e.g.* absence of side reactions with air or mechanical strength of the storage particles – for certain system designs (open/closed and fixed/moving bed).

Most existing domestic heat storage prototypes based on salt hydrates are closed systems that contain a packed bed. In these designs a heat exchanger is embedded within the bed, usually by means of metal plates or fins (Table 2). Only a few existing prototypes employ solid-state heat-storing reactions; most are based on solid-solution transitions, followed by dilution of the salt solution held by capillary forces in porous media. The deliquescence of the salt allows for the extraction of more heat in comparison with solid-state transformation, but at the expense of reduced temperature lift.⁴⁹

TCES for domestic heat storage has not been widely adopted because the primary operating requirements are not yet fully met. For example, typical energy storage densities are $0.3\text{--}0.9\text{ GJ per m}^3$ of bed, and these values are further lowered by the

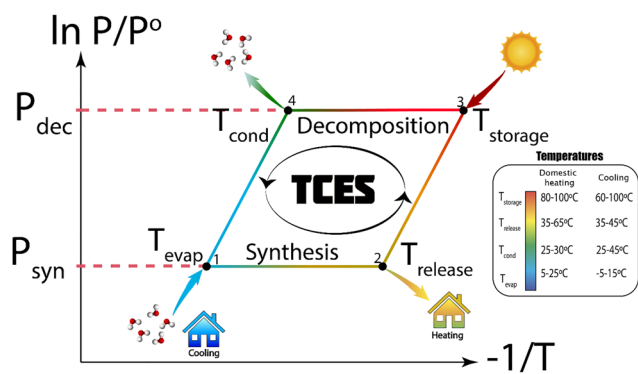


Fig. 3 The four-temperature thermodynamic cycle of a thermally-driven chemical heat pump for domestic TCES depicted in $\ln P/P_0 - (-1/T)$ coordinates with typical temperature values in the inset.



Table 2 Examples of lab-scale prototypes of domestic TCES systems and their most relevant characteristics. Only prototypes releasing heat at $T_{\text{release}} > 30\text{ }^{\circ}\text{C}$ and having temperature lift $>10\text{ }^{\circ}\text{C}$ are included

| Heat release transition | Type | ESD _{mat} /ESD _{bed} , GJ m ⁻³ | Temperatures $T_{\text{evap}}/T_{\text{release}}/T_{\text{storage}}$, °C | TL _{max} , °C | Power, W kg ⁻¹ | N_{cycles} | Ref. |
|--|--------------------|--|--|---------------------------|------------------------------|---------------------|------|
| $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O} \rightleftharpoons \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | Packed bed, closed | 2.0/0.5 | 10/50/130 | 54 | — | — | 339 |
| $\text{K}_2\text{CO}_3 + 1.5\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ | Packed bed, closed | 1.3/0.8 | 10/40/90 | 50 | — | 14 | 340 |
| $\text{SrBr}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} \rightleftharpoons \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ | Packed bed, closed | 2.6/0.67 | 15/35/80 | — | 86.4 (avg) | — | 341 |
| $\text{LiCl} + \text{H}_2\text{O} \rightleftharpoons \text{LiCl solution (vermiculite)}$ | Packed bed, closed | —/1.0 | 10/35/90 | 12 | 2100 (peak) | 14 | 342 |
| $\text{LiBr} + \text{H}_2\text{O} \rightleftharpoons \text{LiBr solution (silica)}$ | Packed bed, closed | 1.37/— | 10/30/120 | 17 | 300 (peak) | 10 | 343 |
| $\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{CO}_3 \text{ solution (vermiculite)}$ | Packed bed, closed | —/0.9 | 25/40/120 | 15 | 450 (avg) | 47 | 344 |
| $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CaCl}_2 \text{ solution (vermiculite)}$ | Packed bed, open | —/0.36 | 20/57/80 | 36 | 106 (peak) | 6 | 58 |

volume of the condenser, pipes, and other components. Unfortunately, energy storage densities at the system level are reported infrequently. For systems that undergo deliquescence, low temperature lift ($<20\text{ }^{\circ}\text{C}$) remains a challenge, while low power is a common limitation for systems employing solid-solid heat-storing reactions. At present, there exists no “best” material or system design for TCES in domestic applications. Rather, every prototype strives to meet performance demands through a combination of design trade-offs. The necessity of these compromises reflects the absence of an ideal TCES material. Developing improved material(s) is one of the main challenges for accelerating the adoption of TCES.

Cooling and air conditioning. Sorptive cooling dates to the work of Michael Faraday, who used ammonia as an adsorbate and AgCl as a sorbent.^{68,69} The thermodynamic cycle for cooling is similar to the cycle for domestic heating (Fig. 3), with two major differences: the useful effect (*i.e.* cooling) occurs during evaporation, and the boundary temperatures can vary depending on the purpose of the cooling.

Typical applications include air conditioning in buildings and in transport (cars, marine vessels), cooling of datacenters, and ice making for food preservation. For air conditioning, $T_{\text{evap}} = 0\text{--}10\text{ }^{\circ}\text{C}$, while $T_{\text{evap}} = -5\text{--}0\text{ }^{\circ}\text{C}$ is used for ice making and deep freezing.⁷⁰ Depending on ambient conditions, the condensation temperature is typically $25\text{--}40\text{ }^{\circ}\text{C}$. T_{storage} and T_{release} are usually within similar ranges as for heat storage: $80\text{--}100\text{ }^{\circ}\text{C}$ and $35\text{--}50\text{ }^{\circ}\text{C}$, respectively.

The two main criteria for material selection for a refrigeration cycle are the specific cooling power of a bed, SCP, (*i.e.*, how fast cold can be produced), and the amount of refrigerant exchanged in a cycle⁷⁰ (*i.e.*, the specific refrigerant uptake, Δw), defined by:

$$\Delta w = w_{\text{rich}} - w_{\text{weak}} \quad (10)$$

where w_{rich} and w_{weak} are the maximum and minimum mass of sorbate, respectively, adsorbed or absorbed during a refrigeration cycle per mass of sorbent (Fig. 4). Other criteria include cyclability and cost.

The preference for high specific cooling power (SCP) limits the use of water as a refrigerant; the saturated vapor pressure of water at $0\text{--}10\text{ }^{\circ}\text{C}$ is too low for fast vapor transport and, therefore, fast heat reallocation. (In principle, water may be used at $T < 0\text{ }^{\circ}\text{C}$ in the form of a salt solution⁷¹). For this reason, the most promising refrigerants are ammonia, methanol, ethanol, CO_2 and some fluorocarbons.⁷² The need for high

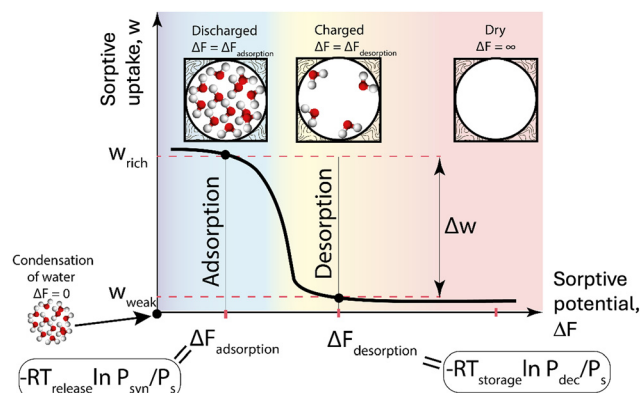


Fig. 4 Representation of the four-temperature adsorptive/desorptive cycle for domestic heating and cooling in w , $-\Delta F$ coordinates.

SCP implies that the sorption process itself should be rapid. The two main sorption mechanisms employed in the TCES field are physical adsorption and absorption of the refrigerant by a salt solution (often in pores of a matrix). Typical SCPs for existing prototypes fall within the range of $300\text{--}1000\text{ W kg}^{-1}$ (Table 3). There is a complex and not yet fully understood interplay of power, layer and heat exchanger geometry, and cycle time, leading to heuristic relations for optimization of such systems.^{73,74}

The connections between adsorbate uptake, pressure, and temperature can be described in terms of the Polanyi sorption potential:⁷⁵

$$\Delta F(T, P) = -RT \ln\left(\frac{P}{P_s}\right), \quad (11)$$

where R is the ideal gas constant and P_s is the saturated pressure of the sorbate at temperature T . For most physical

Table 3 Examples of working pairs for sorptive cooling by salts, based on prototype studies

| Sorbent | Refrigerant | SCP, W kg ⁻¹ | Δw , g g ⁻¹ | Ref. |
|--------------------------------------|------------------------|----------------------------|--------------------------------|-------------|
| CaCl_2 in silica | H_2O | — | 0.75 | 345 |
| CaCl_2 in zeolite + MWCNT | H_2O | 1111 | 0.5 | 346 |
| MnCl_2 in expanded graphite | NH_3 | 350 | 0.54 | 285 |
| BaCl_2 in vermiculite | NH_3 | 300–680 | 0.25 | 286 and 347 |
| LiCl in silica | CH_3OH | 210–290 | 0.6 | 348 |



adsorbents and composites the sorption uptake curve is invariant with respect to sorption potential (Fig. 4). Once the boundary conditions of the cycle are fixed (Fig. 3), the Polanyi potentials required to trigger sorption and desorption can be defined (Fig. 4). An optimal sorbent will exchange a large amount of refrigerant between the two boundary potentials. Typical Δw values are 0.2–0.7 g g⁻¹ for adsorbents such as silica gel, zeolites, and salt composites retained within the pores of a host. Recently, several metal–organic frameworks (MOFs) with high water uptake (up to 2 g g⁻¹, the highest uptake reported to date) were identified as promising for cooling.^{76–78}

Thus, the main challenge for material science in sorptive cooling is the identification of sorbents that can exchange large quantities of adsorbate rapidly and repeatedly under T, P conditions appropriate for the cooling cycle.

Heat and moisture recuperation in ventilation systems. In cold climates, the share of heat loss from ventilation systems can reach ~50%. Hence, one promising niche application for TCES is sorptive recuperation of moisture and heat from ventilation. The operating principle for sorptive heat/moisture recuperation involves sorption of water from outgoing air at room temperature and relative humidity (RH) ~40–50%, followed by heat transfer to the ingoing air by means of a heat exchanger (Fig. 5). The ingoing air (which is heated in the heat exchanger) is moisturized *via* the sorbent bed to recuperate humidity. This process minimizes the freezing of air in the heat

exchanger and allows for the maintenance of comfortable relative humidity indoors.

Climate conditions and the desired indoor RH set the requirements for the sorbents used for heat and moisture recuperation:

- The water affinity of the sorbent must be large enough to ensure deep drying of the outlet air to the ambient dew point, to prevent ice formation at the bed outlet
- Water affinity must be low enough to ensure the release of water to humidify the inlet air to a comfortable RH (40–60%)
- Water uptake, Δw , must be maximized

These requirements can be formulated in terms of the sorption potential, as explained above for sorptive cooling. Currently, traditional adsorbents⁷⁹ (*e.g.* in form of desiccant wheels) and composite sorbents⁸⁰ are considered promising for this application.

Other applications. Other sorptive applications include water desalination⁸¹ and water harvesting from air.⁸² Performance requirements for these cases are typically formulated in terms of the amount of water harvested/produced per unit time. For the materials, this means a large uptake swing Δw between sorptive potentials (Fig. 4), which are in turn defined by climatic or ambient conditions such as temperature and relative humidity. Other requirements are low cost and cycling stability. Recent advances in MOF chemistry have led to the design of adsorbents suited for these applications.⁸³ Unlike zeolites or salts in porous matrices, these MOFs allow for milder regeneration temperatures and greater water uptake.^{84–86}

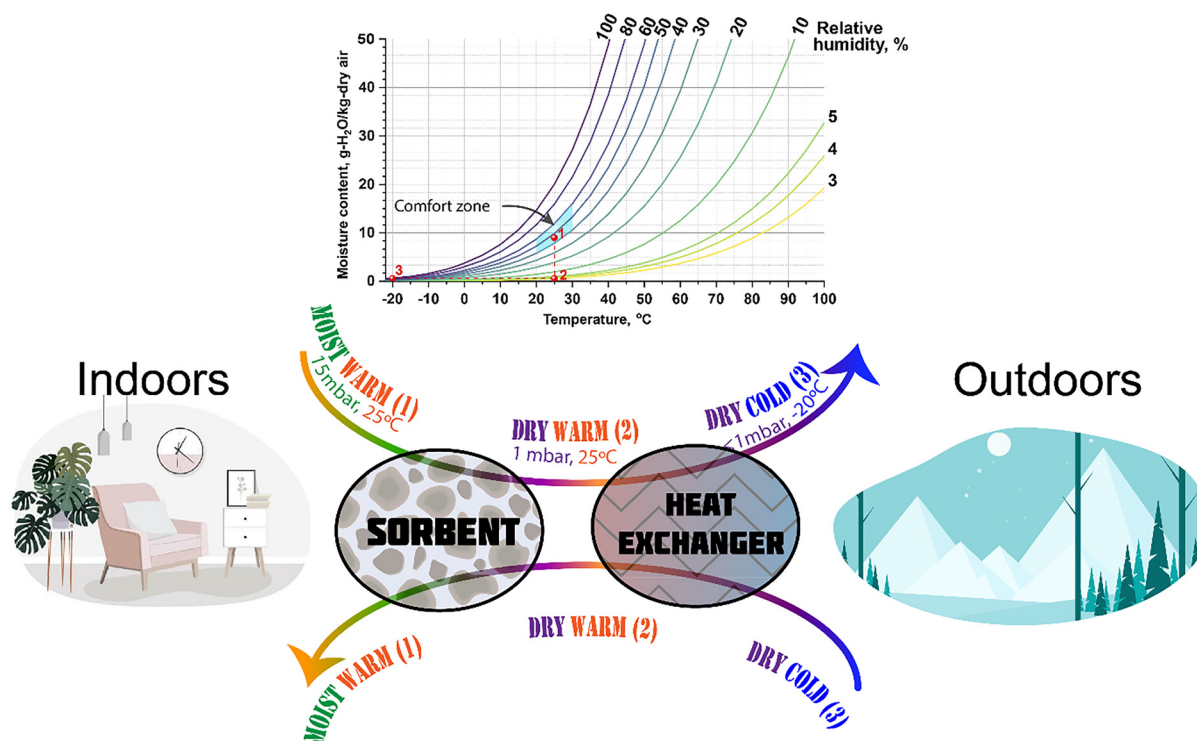


Fig. 5 Ventilation systems. The moist warm air (point 1 on the psychrometric chart) enters the layer of adsorbent to isothermally dry (point 2), then it exchanges the heat with the cold air at point 3 and is exhausted. Conversely, the outside cold air is heated up and moisturized by the sorbent. The indoor comfort zone is highlighted in blue on the psychrometric chart.

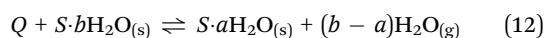


Materials classes and their key attributes

A. Overview of low-temperature thermochemical storage materials

There are three general classes of processes for low temperature thermochemical energy storage. In the first class, a solid chemically reacts with a gas through an absorption process, forming another solid. The most common materials used for this class are salt hydrates, although ammoniates and methanlates operate analogously. The second class consists of the adsorption of a gas within a porous host, such as silica gel, a zeolite, or a MOF. Finally, the third class involves the absorption of a gas by a liquid. The different material families corresponding to these three classes of processes have different properties, which are summarized in Table 4.

In the process, heat is stored in the endothermic decomposition of a more complex solid into another (compositionally simpler) solid and a gas. Heat is released during the reverse synthesis reaction. In the case of salt hydrates (*i.e.*, salts with water molecules incorporated into their crystal structure), the reaction is:

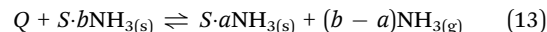


where Q is the heat of reaction, $S \cdot b\text{H}_2\text{O}_{(s)}$ is a salt hydrate, $S \cdot a\text{H}_2\text{O}_{(s)}$ is the dehydrated salt or hydrate (with $b > a$), and $\text{H}_2\text{O}_{(g)}$ is water vapor. The choice of water as the reactive fluid carries several benefits for low temperature TCES, including safety and abundance, as well as favorable thermodynamic properties that allow the (de)hydration reactions to be reversed at relatively low temperatures.

Of the low temperature TCES materials, hydrates tend to have the highest energy densities at the materials level, both theoretically⁸⁷ and experimentally.⁸⁸ However, many salt hydrates display complexities when implemented in practical systems. For example, some hydrates melt (*i.e.*, form concentrated aqueous salt solutions) rather than dehydrate (*i.e.*, release water vapor) when heated. Others deliquesce when the water vapor pressure is too large, *i.e.*, greater than the deliquescence relative humidity (DRH) of the material. Still others will experience side reactions, such as the well-known hydrolysis of lower hydrates of MgCl_2 , which forms gaseous HCl .⁸⁹ All of these phenomena cause irreversibilities that reduce, upon cycling, the amount of active material that can store heat. Furthermore, the complexities of heat and mass transfer in salt hydrates can result in slow kinetics. In addition to these technical issues, some salts are impractical due to their high cost or toxicity. Despite these practical complications, salt hydrates remain a promising class of TCES materials. Much research is being done to characterize and understand their performance at the materials level, and recently some large-scale prototypes using salt hydrates have been built.^{63,90}

Like hydrates, ammoniates are salts with ammonia molecules present within the crystal structure. Salt ammoniates were originally proposed decades ago for TCES, but only recently

have drawn serious attention.^{91–93} The ammoniates are analogues of salt hydrates as they are defined by the reaction:



where the reactive fluid is ammonia rather than water. The use of ammonia poses a practical challenge for many applications as ammonia is toxic. Regardless, these materials may be of interest to a sub-set of applications where the toxicity issue can be managed. Recently, Müller *et al.* characterized many ammoniates according to their energy density.⁹¹ The value recorded in Table 4 has been adjusted to maintain consistency with other entries in the table, where energy densities are reported in terms of the volume and/or mass of the more complex (hydrated or ammoniated) material. Here, it can be seen that ammoniates have comparable, although slightly smaller energy densities than hydrates. Similar to hydrates, ammoniates may experience irreversible side reactions, such as the formation of NH_4Cl in chloride salts.⁹¹ They also require the use of pressurized vessels in system designs, which will increase cost and potentially impact energy densities. However, one potential advantage of ammoniates over hydrates is their faster charging/discharging rates due to higher pressures. This is demonstrated by the power value calculated from data reported by Yan *et al.* for the reaction of MnCl_2 with ammonia.⁹⁴ Finally, since ammoniates have not drawn as much attention as salt hydrates, most ammoniate studies for TCES are on the laboratory scale.

A smaller family of TCES materials in the first class are salt methanlates, which store methanol molecules in the salt crystal structure. Their reaction is defined as:



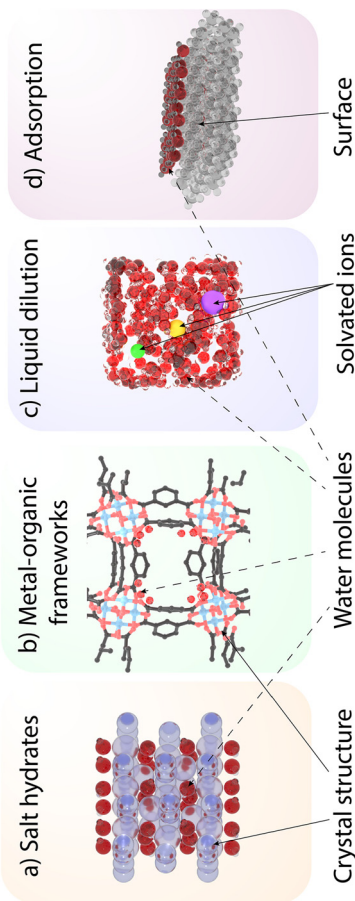
The literature on methanlates for TCES is sparse. Given methanol's favorable properties for refrigeration they are mainly of interest for refrigeration applications.⁹⁵ From the data available in the literature, methanlates appear to exhibit similar (perhaps slightly smaller) energy and power densities compared to salt hydrates.^{96,97} Methanlates tend to deliquesce easily, so porous matrices have been used to stabilize and exploit deliquescence.^{98–101} The main drawback to their use is the flammability and toxicity of methanol.

The second class of low temperature TCES materials are porous media. These materials adsorb a reactive gas onto the surfaces of their pores. In most cases, this gas is water, as water has many favorable properties mentioned previously. The different porous media display a range of pore sizes, classified as micropores (pore diameter < 2 nm), mesopores (2–50 nm), or macropores (> 50 nm).¹⁰² An example of one of the most mature TCES storage materials is silica gel, which consists of mesoporous amorphous silicon dioxide. These pores readily absorb water from the environment, leading to its common use as a desiccant. Advantages of silica gel include its relatively low cost, widespread availability, and good cyclability.¹⁰³ As a result, it has been developed to commercial scale quicker than other thermochemical materials. However, its relatively low



Table 4 Overview of low temperature thermochemical heat storing materials. The illustration shows a few examples of TCES materials, including (a) a crystal structure of a salt hydrate (LiCl·H₂O, Class I), (b) a crystal structure of a MOF (CAU-10, Class II), (c) a cartoon depicting liquid dilution (Class III), and (d) surface adsorption (on quartz (001))

| Class | Material | Energy density | Stability | Power output | Non-technical attributes | Technology readiness level |
|-------|-------------------|---|--|---|---|--------------------------------|
| I | Salt hydrates | Up to 3.8 GJ m ⁻³ and 2.3 MJ kg ⁻¹ ⁸⁷ | Issues with melting, deliquescence, and hydrolysis | Up to 0.7 MW m ⁻³ and 0.5 kW kg ⁻¹ ^{136,155} | Rarity and toxicity vary by salt | Laboratory and prototype scale |
| I | Salt ammoniates | Up to 2.1 GJ m ⁻³ and 1.6 MJ kg ⁻¹ ^{91,94} | Issues with thermal decomposition | Up to 1.5 kW kg ⁻¹ ⁹⁴ | Rarity varies by salt, ammonia is toxic | Laboratory scale |
| I | Salt methanolates | Up to 1.3 MJ kg ⁻¹ ⁹⁶ | Limited data available | Up to 0.4 kW kg ⁻¹ ⁹⁷ | Methanol is flammable and toxic | Laboratory scale |
| II | Silica gel | Up to 0.8 GJ m ⁻³ and 1.4 MJ kg ⁻¹ ³⁴ | Good stability | Up to 0.01 kW kg ⁻¹ (prototype) ¹⁰⁴ | Cheaper | Commercial scale |
| II | Zeolites | Up to 0.7 GJ m ⁻³ and 1.1 MJ kg ⁻¹ ³⁴ | Good stability | Up to 0.03 kW kg ⁻¹ (prototype) ³⁴⁹ | Can be expensive | Commercial scale |
| II | MOFs | Up to 1.3 MJ kg ⁻¹ ¹⁰⁹ | Issues with hydrolysis | Up to 2.1 kW kg ⁻¹ ¹⁰⁹ | Can be expensive | Laboratory scale |
| III | Liquid dilution | Up to 1.4 GJ m ⁻³ ¹¹¹ | Good stability | Up to 0.03 MW m ⁻³ (prototype) ³⁵⁰ | Can be cheaper | Commercial scale |



a) Salt hydrates

b) Metal-organic frameworks

c) Liquid dilution

d) Adsorption

Crystal structure

Water molecules

Solvated ions

Surface



energy density in the operational window of low-temperature TCES limits its potential in compact applications. The low power cited in Table 4 for this material is derived from a large-scale prototype involving 350 kg of silica gel.¹⁰⁴

Zeolites represent another category of material that falls within the second class of TCES media. Zeolites are aluminosilicates that can adsorb water into their micropores. Like silica gel, zeolites have been developed to the commercial scale. They are stable but are costlier than silica gel. They possess slightly smaller gravimetric energy densities than silica gels due to their weight, but higher power densities at the prototype scale compared to silica gels. One characteristic of zeolites is their hydrophilicity, resulting in high desorption temperatures for water.¹⁰³ As such, depending on the maximum charging temperature available, the reversible capacity of zeolites at low temperatures (100 °C) can be limited.

Metal-organic frameworks (MOFs) represent another promising category of porous materials that are of interest for low temperature TCES. MOFs are porous, crystalline materials consisting of metal clusters connected by organic linkers. Well known for their extremely high surface areas, the size of the pores in MOFs can be tuned by substitution of linkers of varying length.¹⁰⁵ Given the many degrees of freedom in MOF structure and composition, the potential chemical space for MOFs is extremely large, which has attracted the interest of materials designers.¹⁰⁶ In addition to their cost, the main disadvantage of MOFs is that some MOFs decompose irreversibly in the presence of water, making reversible water capture and release an impossibility for those compositions.¹⁰⁷ However, several water-stable MOFs are known and show promise for TCES, such as MIL-101, CAU-10, NH₂-MIL-125, MOF-801.⁸⁶ Recent efforts have focused on computationally predicting the water stability of MOFs.¹⁰⁸ Ehrenmann *et al.* characterized the water adsorption of MIL-101, for which energy density and power are reported in Table 4.¹⁰⁹ While the energy density of MOFs is similar to other types of materials, the main advantages are the high power density, which reflects the high degree of regular porosity found in MOFs, and the stepwise adsorption behavior, which, albeit, has been demonstrated only for a few MOFs.¹¹⁰

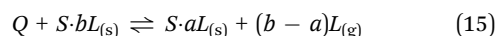
Finally, the third class of low temperature TCES materials operates *via* liquid absorption, in which a solute is reversibly evaporated from/absorbed into a solvent. Evaporation, which concentrates the solute (by desorbing the solvent), is endothermic, while the condensation of the solvent back into solution is exothermic. This approach tends to exhibit good stability and thus has reached commercial scale. Also, depending on the solute chosen, the material cost can be relatively inexpensive. Regarding its energy density and prototype-scale power density, its performance is average compared to other types of materials. Yu *et al.* proposed a three-phase sorption cycle using LiCl/H₂O, where the liquid absorption accounted for 57% of the energy stored, translating to an energy storage density of 1.4 GJ m⁻³ for heat storage.¹¹¹ Another remarkable solute is NaOH with potential storage density exceeding 1 GJ m⁻³ and 20–25 °C temperature lift.⁵⁰ A trade-off between the energy

storage density and the temperature lift is the main reason why absorptive heat storage systems are not yet widespread.¹¹²

B. Class I: salt hydrates, ammoniates, and methanolates

Materials and scales. Before going into details regarding the properties of salts and their interactions with vapor, it is helpful to have a basic understanding of how these materials will be deployed within a thermal energy storage device. In the core of the device will be a storage bed comprised of small particles of the storage material. Since a powder based on very small crystallites will have a poor permeability for water vapor, use of millimeter-sized particles is foreseen. The particles will be manufactured from a powder and themselves be porous in nature. This introduces several length scales as illustrated in Fig. 6, where a cartoon of a hydrating K₂CO₃ particle is shown. The structure and processes occurring at these length scales have distinct contributions to properties like energy density, power, stability, *etc.*

Phase equilibria. Consider a salt that can change its loading with vapor according to the following reaction equilibrium.



Here, S represents a neutral ion pair in the salt. L is the gaseous compound that reacts with the salt: *i.e.* H₂O (hydrates),^{46,47,114} NH₃ (ammoniates),^{115–117} CH₃OH (methanolates),¹¹⁸ C₂H₅OH (ethanolates),¹¹⁸ *etc.* Q is the heat associated with the reaction. During reaction, the salt switches between two states of loading (the number of molecules L per neutral ion pair) a and b with $b > a$. Bonding of the gas to the salt is accompanied by a release of heat. Therefore, increasing the loading of L within the salt ($a \rightarrow b$) takes place with the discharge of heat, while reducing the loading ($b \rightarrow a$) charges the medium. Since the reaction involves a structural change of the crystalline lattice, the process behaves as a phase change. According to the Gibbs phase rule, such a transition occurs at a well-defined set of temperatures T and vapor pressures p , with $p = f(T)$. From here forward we will focus the discussion on salt hydrates, $L = \text{H}_2\text{O}$, but similar considerations apply to ammoniates, methanolates, *etc.* As needed, considerations unique to the ammoniates and methanolates will be discussed separately.

When the reaction shown in eqn (15) is in equilibrium, $\Delta G_{\text{rxn}} = 0$. It follows from this equilibrium condition that the

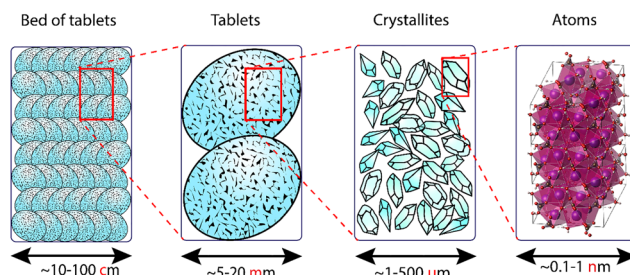


Fig. 6 The different length scales associated with the hydration of K₂CO₃. Reproduced from ref. 113 under the terms of the Creative Commons CC-BY license, copyright 2024.



equilibrium vapor pressure p_{eq} and T are related *via* the van 't Hoff equation.

$$p_{\text{eq}} = p^0 \exp \left[\frac{\Delta H_{\text{ab}}^0 - T \Delta S_{\text{ab}}^0}{RT} \right] \quad (16)$$

where p^0 , ΔH_{ab}^0 and ΔS_{ab}^0 are the standard pressure (1 bar), the standard molar enthalpy of absorption (per mole vapor), and the standard molar entropy of absorption (per mole vapor), respectively. Further, R is the gas constant and T [K] is the absolute temperature. In the case of hydration reactions, the enthalpy and entropy are the molar enthalpy and entropy of hydration, respectively. Typical values for the enthalpy ΔH_{ab}^0 and entropy S_{ab}^0 are 40–80 kJ mol⁻¹ and 140–160 J mol⁻¹ K, respectively.^{87,119}

To illustrate the phase behavior of hydrates a water vapor pressure diagram for MgCl₂ is shown in Fig. 7. MgCl₂ can form multiple hydrate phases ($n = 0, 1, 2, 4, 6, 8, 10, 12$)^{120–124} that are stable at different combinations of temperature and water vapor pressure. The most important of these are for $n = 2, 4$ and 6, which are shown in Fig. 7, with data taken from Derby *et al.*¹²⁵ and Carling.¹²⁶ The higher hydrates ($n > 6$) are not stable at the given conditions. The lines for the lower hydrates $n = 0$ and 1 (not shown) are below the line for the 2–4 transition. At high vapor pressures the salt deliquesces: *i.e.* it absorbs water and liquefies (turns into solution). It is important to stress that a pressure–temperature diagram like Fig. 7 is an intrinsic property of the selected salt.

A driving force for the hydration reaction exists when the chemical potential for water in the vapor phase and water in the solid is unequal.

$$\Delta\mu = RT \ln(p/p_{\text{eq}}) \neq 0 \quad (17)$$

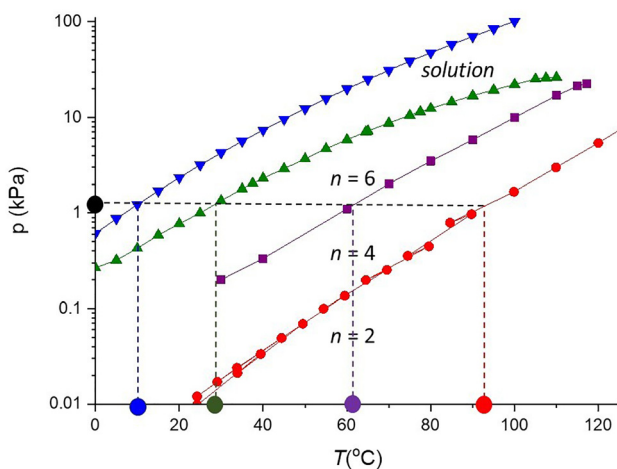


Fig. 7 Water vapor pressure–temperature lines for phase transitions of MgCl₂ hydrates MgCl₂· n H₂O: deliquescence (green), $n = 4 \rightarrow 6$ transition (purple), and $n = 2 \rightarrow 4$ transition (red). The blue line/points refer to the P–T combinations for saturated water vapor. The coloured dots on the abscissa indicate the theoretical output temperatures of the different phase transitions at water vapor generated at 10 °C (12 mbar). Data adapted from Derby *et al.*¹²⁵ and Carling.¹²⁶

Specifically, the salt is hydrated (discharged) when $p/p_{\text{eq}} > 1$ and dehydrated (charged) when $p/p_{\text{eq}} < 1$.

Diagrams like the one shown for MgCl₂ in Fig. 7 are helpful because they demonstrate important aspects of the operation of salt hydrates. First, a strong coupling exists between the use conditions of a heat storage device and the optimal salt. As the phase lines are intrinsic features of the crystalline structure and composition of the salt, they cannot be easily adapted to accommodate the prescribed conditions. For discharge (heat generation) it is extremely important to know the conditions of the water vapor source that comes into contact with the salt. For example, Fig. 7 shows that when MgCl₂ is reacted with saturated water vapor at 12 mbar/10 °C, the resulting reactions can theoretically deliver heat at several temperatures, corresponding to one deliquescence reaction and two distinct hydration reactions. When the 2 → 4 transition occurs, heat at a temperature slightly above 90 °C is released. However, the temperature of the discharge will drop to lower values of ~60 °C at the 4 → 6 transition. In cases where multiple hydration reactions occur for a given salt (*i.e.*, several hydrated phases are stable), the temperature of the generated heat will decrease as one progresses through transitions corresponding to the formation of phases with larger water content. Hence, the use conditions not only determine the kinetics, but also the available heat and thus the effective energy storage density.

The hydration reaction involves risks. At low temperatures, a salt may undergo deliquescence, which can harm the operation of the heat storage device. This complication can be circumvented by avoiding the low temperatures with a system control, or by stabilizing the material to minimize the impact of deliquescence. Despite these stabilization options, extremely deliquescent salts, like LiCl·H₂O (DRH = 11.2%),¹²⁷ LiBr·2H₂O (DRH = 7.75%),¹²⁷ and CaCl₂·2H₂O (DRH = 12.9%),¹²⁸ are not suitable candidates for heat storage based on salt hydration, as decreases in temperature will immediately lead to deliquescence. It should be noted though that exploiting deliquescence is one of the routes to mitigate these risks.^{111,344} While it is possible to boost storage density by exploiting deliquescence, such systems operating with salt solutions require a porous medium to stabilize and, as noted earlier, often suffer from a poor trade-off between storage density and temperature lift.

Temperature lift. While equilibrium temperature lift (eqn (3)) is determined by the transition on the phase diagram dictated by the boundary conditions ($T, P(\text{H}_2\text{O})$) for heat storage and release, dynamic temperature lift (eqn (9)) is determined by the balance between mass transport and heat transport in a TCES material.¹²⁹ The rate of heat release is determined by the rate at which the sorbate reaches the reaction front and the reaction rate, while the rate of heat transport away from the reaction front is determined by diffusive and advective processes. The dynamic temperature lift is closely related to the power density. Mass transport, reaction kinetics, and heat transport are discussed in more detail below.

Energy density. Energy storage density (ESD) is a key property of an energy storage device. Of course, the system ESD is limited by the intrinsic ESD of the material itself: by embedding



the storage material in a system the resulting system ESD will be less than that of the material alone, due to the volume occupied by the system components. Similar arguments hold for specific energy. Given that system-related penalties are unavoidable, it is desirable to maximize the intrinsic ESD of the material. Since the molar enthalpy of hydration H_{ab}^0 of an $a \rightarrow b$ transition is a fixed number, the energy density on the crystal level u_c equals

$$u_c = \frac{N(b-a)H_{ab}^0}{V_{\max}} = \frac{(b-a)H_{ab}^0}{v_b} \quad (18)$$

where N [moles], $V_{\max} = V_b$ [m^3], and v_b [m^3 per mole] are the moles of neutral ionic pairs, the maximal molar volume of the material (mostly V_b), and the molar volume of neutral ion pair in phase b , respectively. Note this formula assumes that in the device only a single hydration reaction is accessible. Eqn (18) demonstrates that materials with large energy densities should exhibit an efficient packing of water molecules in combination with a large hydration enthalpy.

In cases where multiple reactions (involving different degrees of hydration of the salt) can be accessed the energy density may be expressed as:

$$u_c = \frac{N \sum_{ij} \Delta n_{ij} \Delta H_{ij}^0}{V_{\max}} \quad (19)$$

The summation ij runs over all possible hydration transitions and V_{\max} is the maximal molar volume, usually for the highest hydrate considered. H_{ij}^0 and Δn_{ij} are the molar enthalpy and change in degree of hydration during the transition ij . The total change in hydration state is given $\Delta n = \sum_{ij} \Delta n_{ij}$.

Although eqn (18) and (19) provide an upper limit to the ESD, taking into consideration the discussion about the accessibility of phase lines and the use conditions, the system ESD is strongly dependent on the use conditions of the foreseen application. To illustrate this, Table 5 lists the values for the energy densities and output temperatures for use conditions relevant for the built environment (*i.e.*, assuming hydration at 12 mbar and 10 °C, and dehydration at 20 mbar).⁴⁷

When the ambient temperature or relative humidity are not sufficient to deliver water vapor to the storage system at the required vapor pressure, energy may be required to generate additional vapor from liquid water.³⁰ Accounting for this energy reduces the effective ESD, assuming that this energy cannot be recovered upon discharging. Ideally, all the energy required to generate water vapor should be freely extracted from the environment. However, in some applications, such as in environments near 0 °C, this may not be possible.

There are many system-related factors influencing the system-level ESD.¹³⁰ These include bed porosity, internal storage of water, piping, auxiliary equipment, sensible heat losses during operation, *etc.* Here we limit the discussion to the impact of bed porosity and the internal storage of water.

Regarding porosity, the storage system should allow for easy access of water vapor to the salt. For that reason, the storage medium will likely be filled with discrete particles rather than

Table 5 Overview of crystal-level properties of a selection of salts reported as promising TCES materials. The range of possible hydration states (n), energy density for an open TCES system, decrease in molar volume upon dehydration, temperature delivered during hydration (T_{release}), and deliquescence relative humidity are presented for each material. All values are calculated based on water vapor pressures of 12 and 20 mbar for hydration and dehydration, respectively. Data obtained from ref. 47

| Salt | n in Salt- $n\text{H}_2\text{O}$ | Energy density [GJ m^{-3}] | Volume decrease (%) | T_{release} [$^{\circ}\text{C}$] | DRH (%) |
|-------------------------|------------------------------------|---------------------------------------|---------------------|---|---------|
| CaCl_2 | 0–2 | 1.54 | 35 | 63 | 13 |
| K_2CO_3 | 0–1.5 | 1.30 | 22 | 59 | 43 |
| MgCl_2 | 2–6 | 1.93 | 47 | 61 | 33 |
| MgSO_4 | 1–7 | 2.27 | 63 | 24 | 90 |
| Na_2S | 0.5–5 | 2.79 | 60 | 66 | > 34 |
| SrBr_2 | 0–6 | 2.49 | 61 | 48 | 61 |
| SrCl_2 | 0–6 | 2.99 | 62 | 28 | 73 |

with a salt monolith. Incomplete particle packing introduces porosity (typically 30–50%) into the storage bed, reducing the energy density proportionally.⁴⁷ Furthermore, the particles themselves may exhibit internal porosity which further reduces the ESD.¹³¹ Regarding the internal storage of water,^{47,130} in a closed system the water involved in the hydration reaction is not extracted from the environment and must be stored. As the amount of water to hydrate a salt can be large, the volume of the water storage vessel should be accounted for and can significantly reduce the ESD on the system level.

Metastability. Although the thermodynamics of a hydration reaction imply that hydration will occur when and dehydration at $p/p_{\text{eq}} < 1$, there can exist a zone around the equilibrium pressure–temperature line where the kinetics of the reaction are slow: this is referred to $p/p_{\text{eq}} > 1$ as the metastable zone.⁵⁷ Some reactions suffer from large metastable zones, while others with narrow metastable zones demonstrate fast kinetics close to equilibrium. Metastable zones have been observed for many salts, including LiOH ,¹³² BaCl_2 ,¹³³ K_2CO_3 ,^{57,134} Na_2S ,¹³⁵ MgCl_2 ,¹³⁶ CuCl_2 ,⁵⁷ SrBr_2 ¹³⁷ and certain minerals.¹³⁸ In Fig. 8 the implications of a metastable zone for discharge are shown with the help of the phase diagram of K_2CO_3 .⁵⁷ Upon discharge, when water vapor at 12 mbar is supplied the maximum temperature is about 10 °C lower (50 °C) than what is expected in equilibrium (60 °C). Sufficient power is extracted only outside of the metastable zone. Despite numerous reports of metastable behavior,^{57,88} this phenomenon is still poorly understood.

The existence of a metastable zone with poor kinetics has been hypothesized to result from two rate-limiting mechanisms: deliquescence-recrystallization and nucleation. Deliquescence-recrystallization has been introduced to explain poor hydration kinetics of certain salts in regions of the phase diagram where the thermodynamics favor hydration. For example, the hydration rates of Na_2SO_4 and $\text{Mg}(\text{ClO}_4)_2$ dramatically increase when the water vapor pressure exceeds the point at which the original (lower hydrate phase) deliquesces.^{139,140} The idea is that an $a \rightarrow b$ hydration process follows two steps: deliquescence of the lower hydrate phase, a , followed by crystallization of the higher hydrate phase, b .



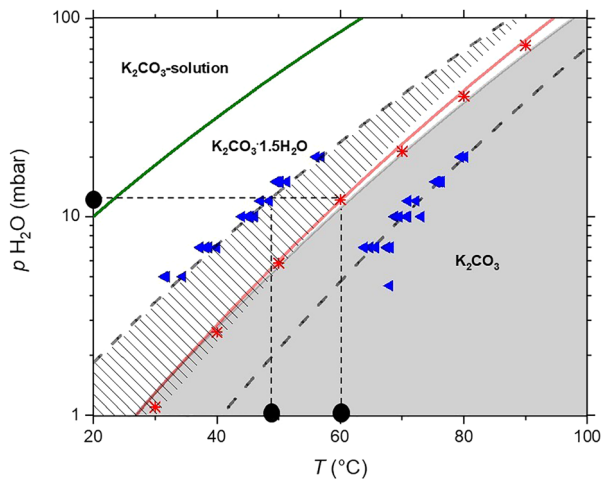


Fig. 8 Phase diagram of K_2CO_3 illustrating its metastable zone. The red and green lines refer to the hydration transition and deliquescence line, respectively. The red and blue data points refer to measurements of the hydration–dehydration equilibrium and the metastable zone boundaries. Data adapted from ref. 57.

However, predictions for the deliquescence points of anhydrous K_2CO_3 and CuCl_2 demonstrated that this hydration mechanism could not explain metastability for these two salts.⁵⁷ In the same study it was shown that the hydration rate of these salts was slowed down due to sluggish nucleation of the hydrate phase. This explanation was proposed decades ago¹⁴¹ for the dehydration of salts. When metastability is explained using classical nucleation theory (CNT), the boundaries of the metastable zones are the points where the critical nucleus size becomes on the order of a neutral ion pair and/or the free energy barrier for nucleation is comparable to the thermal energy:⁵⁷ $\Delta G^\ddagger/k_{\text{B}}T \sim 1$.

As hydration–dehydration processes are solid–solid transitions involving significant modifications to the crystalline lattice, mobile intermediate phases could play a role in controlling the rate of the reaction. Therefore, CNT alone is likely insufficient to explain the origins of metastability. In the case of the hydration transition $a \rightarrow b$ a natural source for ionic mobility could be the surfaces of the relevant crystalline phases. Studies on NaCl have reported the presence of water layers on the crystalline surface far below the deliquescence point of NaCl (DRH = 75%).^{142,143} Furthermore, in these layers there is significant ionic mobility, implying local dissolution processes.^{144,145} Some reports indicate that similar processes might occur on the surfaces of salt hydrates,^{146,147} potentially facilitating the hydration process. It may be expected that the ion mobility on the surface of an ionic crystal will strongly increase with the applied water vapor pressure. In recent studies the existence of such a mobile layer has been proven with the help of electrical impedance spectroscopy.¹⁴⁸ Related to this, extreme deliquescent salts have successfully been used to decrease the metastable zone and/or increase the reaction rate.^{149–151} These surface processes, in combination with a nucleation barrier, could contribute to the metastable zone.

Hence, the metastable boundary for hydration might not only be determined by the disappearance of a nucleation barrier, but also by the presence of sufficient water molecules at the surface allowing for increased ion mobility.

Kinetics and power. The power delivered by a salt hydrate-based storage system relies upon the rate of the underlying hydration–dehydration reaction. In the previous section metastability due to sluggish nucleation and surface effects were introduced as factors influencing these rates. Here, the kinetics of the material outside the metastable zone are discussed. Although many kinetic studies have been published,^{29,152,153} the complexity of these reactions has limited the development of mechanistic insight: crystalline lattices must be restructured, water molecules must be incorporated (hydration) or extracted (dehydration) from the lattice, water molecules must migrate through solids, *etc.*

Based on Fig. 6 the hydration reaction can be thought of as consisting of two steps: (a) diffusion of water vapor through the particle's pore space to the reaction zone, and, (b) transformation of the crystal lattice during simultaneous insertion of water. While the first process occurs at length scales comparable to the particle diameter, the second process occurs at nanometer length scales. Below we briefly summarize the current understanding of these processes.

As an example of a solid–gas reaction,¹⁵⁴ the rate of a hydration–dehydration reaction X can be expressed as:

$$\frac{dX}{dt} = k(T)f(X)h(p/p_{\text{eq}}) \quad (20)$$

Here, $k(T)$, $f(X)$ and $h(p/p_{\text{eq}})$ are, respectively: a temperature dependent reaction constant that can be coupled with an energy barrier, a function describing the reaction pathway, and a driving force term related to the water vapor pressure. Examples of studies using this model to fit the hydration kinetics of salts and salt composites are abundant.^{137,153,155,156} What most studies overlook is that the equation is an attempt to decouple the reaction pathway $f(X)$ from the driving force $h(p/p_{\text{eq}})$ and the intrinsic rate $k(T)$. However, in the case of salt hydration, one might expect that the water vapor pressure can influence both the rate and the reaction pathway. For example, (and as discussed above), with increasing water vapor pressure the amount of adsorbed water at the surface of an ionic solid increases^{142,143,157} and can enhance surface (reaction) mobility.¹⁵⁸ Transition State Theory¹⁵⁹ gives the best justification for using eqn (20) for local hydration/dehydration processes and the most rigorous derivation of the functional relationship of $h(p/p_{\text{eq}})$,¹⁵⁶ but fails in describing many kinetic aspects of salt hydration.¹⁶⁰ Presently, the model is mainly useful for parameterizing the kinetics of salt hydration on a powder level as input for models to describe the kinetics of porous salt particles.

In larger salt particles, the diffusion of water vapor to the reaction zones can impact the reaction rate. The relative importance of this diffusion process can be estimated with the second Damköhler number, $\text{Da}_{\text{II}} = (k_{\text{R}}L^2)/D$, where k_{R} , L , and D are the reaction rate, size of the particle, and the diffusion



constant in the particle, respectively. For millimeter size K_2CO_3 particles $\text{Da}_{\text{II}} > 1$ and diffusion thus limits the reaction rate and power output of the particle,¹³¹ allowing modelling with the Shrinking Core Model.¹⁶¹ The following equation holds for the conversion rate in 1D.¹³¹

$$\frac{dX}{dt} = \frac{M_a D}{(b-a)\rho_a(1-\phi_a)L^2 RT} \left(\frac{1}{X}\right) (p - p_{\text{eq}}) \quad (21)$$

In this model ρ_a , ϕ_a , and M_a are the density, porosity, and molar mass of the starting phase. Note that eqn (20) can be mapped onto eqn (21) with the substitution $h = p - p_{\text{eq}}$ and $f = X^{-1}$. Eqn (21) demonstrates the key factors for understanding and improving the power of TCES particles. Firstly, the power decreases with the extent of the reaction: $dX/dt \propto X^{-1}$. Secondly, the power can be increased by reducing the particle dimensions: $dX/dt \propto L^{-2}$. Based on these findings, models for the hydration of particle beds have been developed.^{162,163}

Degradation. Robustness with respect to degradation of the storage material is also important for the (long-term) performance of a storage device. Three considerations related to degradation are important: first, side reactions during materials manufacturing and use are generally undesirable and should be avoided, as they can compromise energy density and can lead to safety concerns. Second, humid conditions should be avoided during production as deliquescence can hinder the performance of the salt. Third, volume expansion of the salt should not block access of water vapor as this leads to a drop in power output. These three aspects are described in more detail below.

First, in selecting salt hydrates, assessing chemical stability under use conditions is a necessary step. Several examples can be found in the literature that emphasize this point. Na_2S has been considered as a storage material due to its high energy density.^{164,165} Unfortunately, it readily reacts with CO_2 and forms Na_2CO_3 with emission of H_2S .^{136,166} These reactions make Na_2S particle manufacturing a cumbersome process, restricts its use to pure water vapor conditions, and involves a safety risk due to the toxicity of H_2S . Similarly, MgCl_2 is still a widely studied material in the field of thermochemical energy storage,^{153,167-169} despite the fact it is prone to hydrolysis reactions leading to HCl formation¹⁷⁰⁻¹⁷² even at relatively low temperatures.¹³⁶ Similar hydrolysis reactions are known for other halides like CuCl_2 ,^{173,174} MgBr_2 ,¹⁷⁵ and carnallite KMgCl_3 .^{176,177} Further, metal ions that are prone to oxidation by air (e.g., Fe^{2+} , Cr^{2+} , Mn^{2+} , I^-) should be avoided.⁴⁷ Less stable anions (i.e., ClO_4^- , NO_3^-) should also be treated with care.^{46,47}

Second, deliquescence presents a challenge for hygroscopic salt hydrates. A salt or salt hydrate's tendency to deliquesce is characterized by the deliquescence relative humidity (DRH). When the RH of the environment exceeds the material's DRH, the material will deliquesce, i.e., it will spontaneously absorb water from the atmosphere and dissolve within it, forming a liquid solution. Hygroscopic salts/hydrates are characterized by a low DRH. Generally, deliquescence results in reduced cyclability and reaction kinetics due to agglomeration when

liquefied.¹⁷⁸ While this tends to hold true for many salt hydrates, some mixed salt hydrates have demonstrated good cyclability when deliquesced.¹⁷⁹ Furthermore, while hygroscopic salts require more care regarding their stability with respect to deliquescence, these salts also tend to have faster hydration kinetics (below the DRH of the hydrated phase) due to the mobility of the resulting wetting layer.⁵⁷

Third, the volume expansion of the heat storage material is a source of performance degradation in TCES systems. When a salt hydrates and dehydrates, it undergoes considerable volume expansion and contraction.¹⁸⁰ According to the Thermodynamic Difference Rules,¹⁸¹ the relative volume expansion during hydration from $a \rightarrow b$ can be approximated as:

$$\frac{\Delta V}{V_0} \approx (b-a) \frac{v_w}{v_a}, \quad (22)$$

where ΔV is the volume change, V_0 is the volume of the dehydrated phase, v_w is the average specific volume of water in a salt hydrate (similar to the specific volume of ice), and v_a is the specific volume of the dehydrated phase.

Fig. 9 presents the relative volume expansion for selected salt hydration reactions.⁴⁷ A trade-off exists with respect to volume expansion. When a salt undergoes a large volume expansion, many water molecules are typically absorbed in the hydrate (eqn (22)). As shown in eqn (18) and (19), a large difference ($b - a$) results in a larger energy storage density. However, a large volume expansion poses greater risk to the mechanical stability of the salt hydrate. Large volume expansion/contraction can create voids and cracks in the material as it is repeatedly hydrated and dehydrated, resulting in mechanical wear on the system. The material in a TCES reactor will expand over cycling, leading to a porosity reduction of the

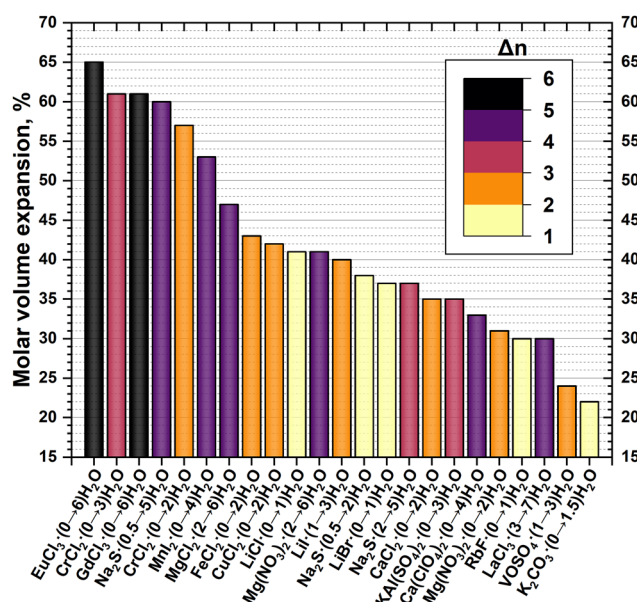


Fig. 9 Relative volume expansion during hydration for representative salt hydrates. The numbers in parentheses indicate the range of hydration states (n in Salt- n H_2O) accessed during the hydration reaction. Δn is the number of water molecules absorbed. Data adapted from ref. 47.



bed.¹⁸² This leads to a reduction of the permeability of the bed, which compromises the working of the TCES reactor.¹⁸³ Furthermore, these voids can affect the kinetics of the reaction. Negatively, the voids reduce the contact area with heat exchanging elements, resulting in lower heat transfer. Positively, the voids increase the porosity of the material, increasing local mass transfer on a particle scale.

One of the major challenges with salt hydrates is to make them stable upon cycling. There are several approaches reported in the literature: encapsulation, matrix stabilization and impregnation of porous media. A review of this topic is beyond the scope of this paper and for this we refer to the recent literature.¹⁸⁴ Prolonging the cyclability of salt hydrate particles is of utmost importance to make salt hydrates viable for the application. It is the opinion of the authors that a breakthrough at this point has not been achieved so far.

Synthetic salts. In recent years there have been several attempts to synthesize new salt hydrates. Especially the sulphate based Tutton salts seem to be a versatile class of materials as the composition of these materials can be changed, which allows for targeted design of the phase diagram of these salts.^{185–187} Sulphate based Tutton salts have a chemical formula $M_2M'(SO_4)_2(H_2O)_6$, where M^+ and M'^{2+} are two different cations. Just like with the regular sulphate and phosphate salts, the major challenge with these salts is in the reversibility of the hydration/dehydration reaction.

Thermal properties. The power output of a TCES device depends on the rates of mass and heat transfer during the chemical reaction. Thus, high thermal conductivity is desirable within the heat storage medium to allow for rapid heat transfer. Unfortunately, many TCES materials exhibit low thermal conductivities. Thermal conductivities for salt hydrates fall within the range of $0.3\text{--}1.3\text{ W m}^{-1}\text{ K}^{-1}$.^{188–191} This is much smaller than that of metallic conductors such as Al and Cu, whose values are roughly $200\text{--}400\text{ W m}^{-1}\text{ K}^{-1}$. Thermal conductivity tends to increase with the hydrate number,¹⁹¹ indicating a greater thermal limitation in the dehydrated phase. The use of composite materials, such as a salt hydrate embedded in expanded graphite, has been used to increase the thermal conductivity of the material.^{192,193} This approach incurs a trade-off between thermal conductivity and energy storage density, as the energy storage density of the overall material decreases as more of the thermal conductivity enhancing material is used. Thus, TCES system designs must strike a balance between energy storage density and power density.

Scarcity, cost, and toxicity. Non-technical aspects such as scarcity, cost, and toxicity can impact the practicality of a TCES material. The importance of these factors can be illustrated with a simple calculation focusing on the built environment in Europe. In 2019 the population of the EU was about 513 million¹⁹⁴ people living in approximately 223 million households.¹⁹⁵ Let us assume that each of these households owns a 2 GJ thermal storage unit, and that the typical energy density at the materials level is $u_c = 1\text{ GJ m}^{-3}$, with a materials density of 1000 kg m^{-3} . For this scenario approximately 400 million metric tons of storage material is required. Although

this is a simple estimate, it demonstrates that significant demand for TCES materials may be expected. This increase in demand mimics the dramatic increase in the supply of raw materials required for widespread adoption of more mature energy technologies (PV, wind turbines, and batteries).¹⁹⁶

Although the price of a given salt on the bulk market serves as one indicator of scarcity,⁴⁷ this approach is not predictive of future demand and associated costs.¹⁹⁶ An analysis that accounts for known resources, mining capacities, and production capacities for synthetic salts would be more useful in assessing scarcity. Although elements such as K, Na, and Ca are abundant, limiting factors for using salts containing these elements are the mining capacities for specific minerals or the production capacities in the case of synthetic salts (*i.e.* K_2CO_3 and Na_2S). Furthermore, many salts under investigation contain minerals that should be treated with care in view of resources and mining production. Fig. 10 illustrates resource and mining data from the U.S. Geological Survey for elements frequently considered in studies of TCES materials.¹⁹⁷ These materials quantities are compared to the 400 million ton estimate for widespread use of thermal energy storage in Europe.

First, let us consider the data presented in Fig. 10 for lithium. Although lithium salts are promising for thermochemical energy storage,¹⁹⁸ lithium already plays a key role in the electrification of energy systems due to its use in Li-ion batteries. While the abundance of lithium is high (estimated mining resources in 2020 were 86 million tons¹⁹⁷), its use as a key ingredient for both electrical and thermal energy storage devices presents challenges. Considering the production capabilities of Li, Fig. 10 shows that in 2020 the global annual mining production was about 82 000 tons.¹⁹⁷ This is orders of magnitude lower than is expected to be needed for global implementation of Li-based thermal energy storage systems. In view of the growing demand for Li-ion batteries (which is expected to cause a 40-fold increase in Li supply by 2040¹⁹⁹) and the emerging strain this has induced on the global market, it is fair to ask whether TCES should also employ Li-based media.

Salts based on rare earth metals should also be treated with care. In light of the available resources and the present mining production volumes, Fig. 10, the use of lanthanum (*i.e.* $LaCl_3$ ³⁹ and $La_2(SO_4)_3$),²⁰⁰ yttrium (*i.e.* $Y_2(SO_4)_3$)²⁰¹ and vanadium containing salts are of questionable long-term viability. Similar reasoning can be applied to sulphate salts based on elements such as Sc, Yb, Y, Dy, Ga and In.²⁰¹ On the other hand, strontium-containing salts deserve attention in view of their substantial annual mining production. $SrBr_2$ and $SrCl_2$ are considered promising as they have suitable thermodynamic properties.^{39,137,202} However, mining and production capacities will need to be increased for these salts to become practical ingredients in future heat storage systems.

As discussed above, costs can be high to source materials that are not in wide use. One may expect these higher costs to apply to materials needed for new technologies such as the TCES materials discussed here. Nevertheless, rapid cost reductions have been demonstrated in related technologies by



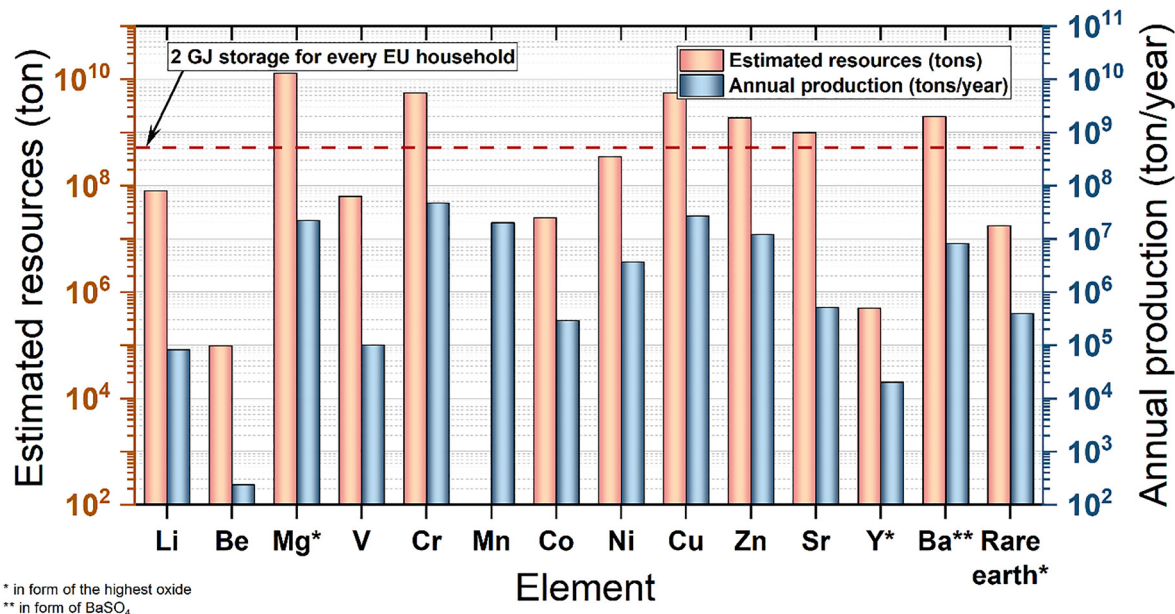


Fig. 10 Estimated resources (left axis) and global annual mining production (right axis) in 2023–2024 for elements that frequently appear in studies of thermochemical energy storage. The dashed red lines mark the 400 million tons of material needed for a use scenario in which all EU-households operate a 2 GJ thermal storage unit. Data is from the U.S. Geological Survey.¹⁹⁷

exploiting economies of scale. For example, the cost of Li-ion batteries has decreased by approximately 97% over the past three decades.⁶⁰ We anticipate that similar cost reductions can be achieved for the materials relevant for TCES.

Toxicity is another important factor for salt hydrates.^{39,47,203} A screening study of 125 salts focusing on safety issues highlighted that 80 salts exhibit challenges due to toxicity.³⁹ For similar reasons, an assessment of medium-temperature heat storage applications urged caution in the use of compounds containing ions like Cr⁶⁺, Co^{2+/3+} and Ni^{2+/4+}.²⁰³ An assessment of 563 hydration reactions (later extended to 1073 reactions⁴⁸) for the built environment (hot tap water and space heating) generated a list of 25 candidates with suitable thermodynamic properties (energy density and discharge temperatures). In this case salts such as GdCl₃, NiCl₂, Na₂S, MnI₂, VOSO₄ and CuCl₂ were excluded due to toxicity considerations.⁴⁷ Hence, substances such as CrF₃ and CuBr₂, identified as promising based on their hydration enthalpies,⁸⁷ warrant additional care in their manufacture and use due to toxicity considerations.

The above considerations suggest two conclusions: first, investments in mining and production capabilities are needed to facilitate global adoption of salt hydrate heat batteries. Secondly, more detailed knowledge of the non-technical features of these materials will be helpful to material scientists in the selection of appropriate materials.

Computational discovery of salt hydrates. Computational modelling has also been employed to investigate materials for TCES. In a trio of studies,^{87,204,205} Kiyabu *et al.* used Density Functional Theory calculations to predict the energy densities and turning temperatures of salt hydrates and hydroxides. In the first study,⁸⁷ 265 hydration reactions were examined for all the halide hydrates and hydroxides present within the

Inorganic Crystal Structure Database (ICSD). Promising reactions having high gravimetric and volumetric energy densities were identified and categorized according to their operating temperatures. Of these, CrF₃·9H₂O was highlighted as a promising under-explored material for moderate-temperature TCES applications ($T \sim 200$ °C). Using this database of calculated properties, property-performance relationships were examined across the hydrates and hydroxides using a Pearson correlation matrix. In the hydroxides these analyses identified the ionicity of the cation-hydroxide bond as a good predictor of the enthalpy of reaction. However, similar (linear) correlations did not emerge in the hydrates, suggesting that more flexible models were needed to predict the thermodynamics in this class of materials.

Kiyabu *et al.* subsequently expanded their screening of TCES materials to include a larger collection of hypothetical salt hydrates, including 5292 metal halides²⁰⁴ and 7012 salts containing chalcogenides and complex anions.²⁰⁵ From these datasets, the hydrates of several salts, including CaF₂, VF₂, CoF₃, Li₂S, Ca(OH)₂, and Li₂CO₃ were identified as potentially new TCES materials with class-leading energy densities and operating temperatures suitable for use in domestic heating and intermediate-temperature applications. Fig. 11 illustrates energy densities for the subset of the screened metal halides that were predicted to be stable with respect to competing phases at all stages of their respective hydration/dehydration reactions. The performance of these materials was projected to the system level by parameterizing an operating model^{90,165,206} of a solar thermal TES system with data from the new hydrates. Finally, machine learning models were developed to predict salt hydrate thermodynamics and identify design guidelines for maximizing energy density. These models demonstrate that



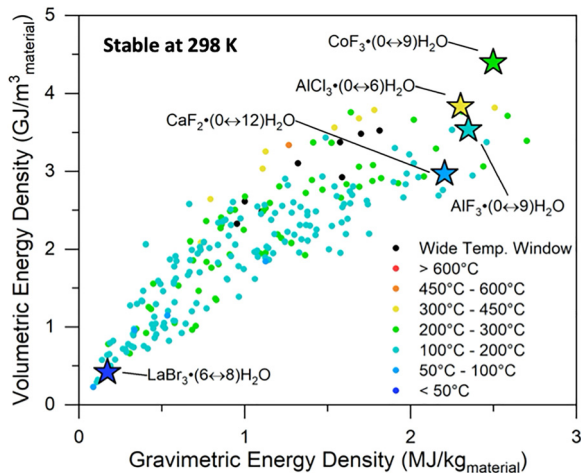


Fig. 11 Volumetric energy density, gravimetric energy density, and temperature category for 238 TCES reactions involving new hypothetical salt hydrates. Promising reactions in distinct temperature categories are shown as stars. All of these hydrates, as well as all intermediate phases present during (de)hydration, are predicted to sit on the convex hull, and thus to be stable with respect to the formation of other phases at 298 K. Adapted from ref. 204 with permission from the American Chemical Society, copyright 2022.

salts composed of cations that exhibit small electronegativities and molar masses (*e.g.*, Na^+ and K^+) yield increased energy densities *via* increased ΔH of hydration. For complex anion hydrates, the identity of the anion was also found to be a significant predictor of ΔH : a greater elemental fraction of nonmetals was found to correlate with a greater ΔH .

C. Class II: porous media/sorption

Porous solid adsorbents constitute a well-established class of thermal energy storage materials that have been considered for use in heat pumps and chillers. Prominent examples of this

class include activated carbon, silica gel, zeolites, activated alumina oxide, covalent organic frameworks (COFs), and metal organic frameworks (MOFs). These materials store heat by exploiting the heat of adsorption of the working fluid vapor. Recent developments have demonstrated remarkable performance improvements, with advanced COF materials achieving thermal conductivities exceeding $15 \text{ W m}^{-1} \text{ K}^{-1}$,²⁰⁷ while novel MOF-salt composites have reached ammonia storage capacities of 48.3 mmol g^{-1} .²⁰⁸ The working fluid can be condensed during the storage/release cycle (*e.g.* water, ethanol, methanol, ammonia); alternatively, non-condensable gases are used, the most common of which are CO_2 and H_2 .

A combination of material-level (*i.e.*, chemical composition, textural/crystallographic, thermodynamic, and kinetic) and system-level (*i.e.*, packing density, vapor transport, thermal conductivity, *etc.*) properties determine the performance of an adsorption-based TCES system (Fig. 12). In general, textural and crystallographic properties such as specific surface area, pore volume, pore size and distribution, and single crystal density determine the amount of working fluid adsorbed by the porous host at a certain sorption potential (Fig. 4). Hence, the structure of the adsorbent strongly influences the capacity for heat storage. On the other hand, the operating temperature window is partly determined by the enthalpy of adsorption and its dependency on sorption uptake, which itself is strongly influenced by the composition of the adsorbent/adsorbate pair through the nature of the bonds formed between host and guest atoms.

Criteria for selecting adsorbents. The selection of porous adsorbents for TCES is guided by the operating conditions of the intended application. As described below, the application places constraints upon the adsorbent's operating temperature range, storage capacity, and its kinetics.

Adsorbent-adsorbate working pair. The selection of the working fluid is a critical design factor of an adsorbent-based TCES system. The selection criteria for a suitable working fluid

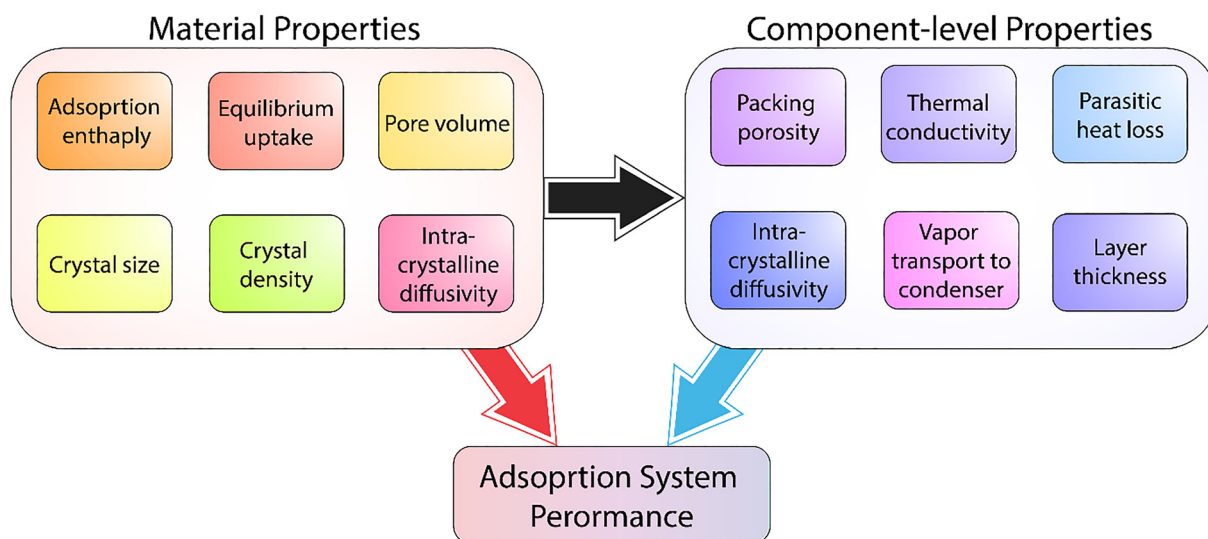


Fig. 12 Performance and efficiency of porous materials-based TCES systems depends on both material-level and system-level property optimizations. Reproduced from ref. 229 with permission from the American Chemical Society, copyright 2019.



include: a high enthalpy of evaporation, condensability under operating conditions, moderate vapor pressure, and being pollution free, non-toxic, and non-corrosive to the system components.²⁰⁹ Water is a popular choice of working fluid due to its abundance, low cost, and non-toxic nature. Water is currently used commercially with zeolites and silica gel adsorbents.^{209,210} However, water is not suitable for subzero temperature applications due to ice formation and freezing issues. Ethanol and methanol have been adopted as alternatives in MOF-based systems to overcome this limitation. Recent simulations and experiments demonstrated high working capacities and COPs in ethanol/MAF-6 systems.²¹¹ Advanced composite working pairs have emerged that significantly outperform traditional systems. For instance, vermiculite/LiCl systems demonstrate superior thermal performance with COPs of 0.75 for cooling and 1.51 for heating, alongside specific cooling performance of $5760.7 \text{ kJ kg}^{-1}$.²¹² Zeolite-based composites, 13X/MgSO₄-LiCl, have also shown substantial improvements, exhibiting higher energy density than pure zeolite 13X and achieving heat storage capacities of 458.3 kJ kg^{-1} .²¹³ Hydrogen²¹⁴ and classical freons²¹⁵ are also used as working fluids in specific systems.

The selection criteria for adsorbents are governed by thermodynamic boundary temperatures and equilibrium vapor pressures for adsorption and desorption.

Adsorption isotherms. The adsorption isotherm quantifies the capacity of a given adsorbent to uptake a working fluid as a function of pressure at a constant temperature, Fig. 13. So-called “S-shaped” or stepwise isotherms are desirable for achieving high working capacity and second-law efficiency.⁷⁰ The International Union of Pure and Applied Chemistry (IUPAC) classifies this family of isotherms as Type V.²¹⁶ The stepwise adsorption typical of a Type V isotherm facilitates the storage of a large quantity of energy within a relatively small change in pressure.^{209,217,218} Recent experiments comparing water adsorption isotherms across Zeolite-Y, activated carbon,

silica gel, and AQSOA™ variants confirm the significance of isotherm steepness and step pressure. For example, AQSOA-Z01 and -Z02 demonstrate sharper S-shaped isotherms at $P/P_0 \approx 0.15\text{--}0.35$, enabling better utilization of low-temperature driving heat.²¹⁹ New MOFs such as KMF-1 and KMF-2 are engineered to produce Type V water isotherms centered at relative pressures $\sim 0.13\text{--}0.2$, with corresponding volumetric energy densities up to 330 kWh m^{-3} .²²⁰ Recent data show MOFs like MIL-125(Ti)-NH₂ exhibit Type V isotherms with high water uptake at relative pressures of 0.1–0.4, ideal for cooling and heating applications.²²¹ For water-based TCES systems, the hydrophilicity or hydrophobicity of the adsorbent governs the shape of the adsorption isotherm: hydrophobic adsorbents often exhibit Type V isotherms. In addition, the volumetric capacity (*i.e.*, the mass of working fluid adsorbed per unit volume of adsorbent), is related to the crystal density and influences the size of the TCES system.

Heat of adsorption. The isosteric heat of adsorption (IHA) is a measure of the strength of interaction between molecules of the working fluid and the adsorbent at a fixed adsorption uptake.^{222,223} In computational studies, this quantity is commonly referred to as the differential enthalpy of adsorption, and is typically derived from Monte Carlo simulations. This interaction determines the hydrophilicity or hydrophobicity of the adsorbent and the regeneration temperature. Recent work suggests that the ideal IHA range for water adsorbents lies between $45\text{--}60 \text{ kJ mol}^{-1}$, balancing high working capacity with low-temperature desorption.²²⁴ For example, KMF-2 achieves an IHA of 40.7 kJ mol^{-1} and can be regenerated at $70 \text{ }^\circ\text{C}$, enabling integration with solar or waste heat sources. A more exothermic IHA leads to a greater amount of energy stored per adsorbate molecule and to a higher regeneration temperature. In addition to the composition of the working fluid and adsorbent, the IHA depends on the size, shape, and polarity of the adsorbate molecules, and on the amount of the working fluid adsorbed (*i.e.*, uptake). IHAs are known to be more exothermic for the adsorption of polar working fluids (*e.g.*, water, ethanol, ammonia) at coordinatively unsaturated metal sites in MOFs. For example, MIL-100(Fe) and MIL-125-NH₂ achieve IHAs supporting energy densities of $\sim 875 \text{ MJ m}^{-3}$ and $\sim 1100 \text{ MJ m}^{-3}$, respectively,²²¹ making them promising candidates for compact thermal storage systems. Thus, the IHA defines the first-law efficiency and the COP. The optimal IHA depends on the application and operating conditions of the TCES system. It should also be noted that, due to the divariance of the adsorption equilibrium, the IHA is often presented as a function of the adsorption uptake.

Regeneration temperature. The temperature at which the adsorbed working fluid molecules are desorbed from the porous host determines the second-law efficiency and cyclability of a TCES system. Ideally, a low ($<100 \text{ }^\circ\text{C}$) regeneration temperature is preferable for domestic, solar, and industrial waste heat-based TCES systems.²²⁵

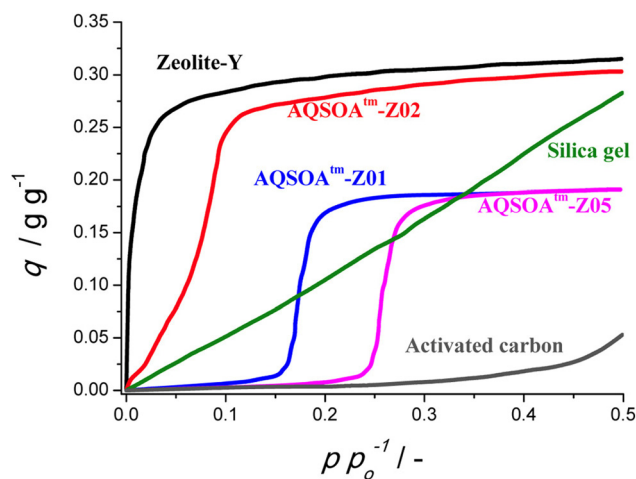


Fig. 13 Adsorption isotherms for water in common commercially available adsorbents. Reproduced from ref. 209 with permission from the American Chemical Society, copyright 2015.



Heat and mass transport. The performance of an adsorbent-based TCES system also depends on the rates at which heat and mass can be transported through the sorbent bed. These properties depend upon *intra*-crystalline and *inter*-crystalline diffusivities (Fig. 12).^{85,209,226} Fick's law^{85,227} is often used to estimate intracrystalline diffusion – *i.e.*, vapor diffusion within single crystals of porous materials – of the working fluid vapor, which in turn allows for modelling of sorption kinetics within porous media using the linear driving force model.^{85,226,228} Due to their crystallinity (and thus lower tortuosity), MOFs are anticipated to exhibit advantages in mass transport compared to non-crystalline hosts such as activated carbons and zeolites. In contrast, intercrystalline diffusion – *i.e.*, vapor diffusion through the interstitial regions between crystallites or particles of the adsorbent – depends on the size, shape, and packing densities of the adsorbent crystals/particles.^{229,230}

One transport-related challenge associated with the use of porous TCES materials such as MOFs is their low thermal conductivity.^{231–233} Hence improving the rate of heat transport through the storage bed may require the addition of thermally conductive additives,^{234–236} which can degrade the effective energy density and possibly slow down the mass transport. However, recent progress in materials design has demonstrated progress in overcoming this limitation. For example, three-dimensional COFs have demonstrated thermal conductivities exceeding $15 \text{ W m}^{-1} \text{ K}^{-1}$, which is the unique performance for 3D polymers.²³⁷ These improvements stem from the optimized structural parameters, particularly small pore sizes around 0.63 nm, four-connected nodes, and material densities above 1.0 g cm^{-3} .²³⁸ In addition, interpenetrated COFs enhance performance through phonon hardening mechanisms, achieving

up to 6-fold thermal conductivity improvements.²⁰⁷ Achieving optimal performance in an adsorption-based TCES system thus depends on both materials-level and system-level design considerations.

Discovery of promising adsorbents. In 2017, Boman *et al.*²³⁹ assessed 110 and 81 adsorbent/adsorbate working pairs for cooling and heating applications, respectively. They identified several MOF-ethanol pairs that outperformed other pairs for heating applications, and additional activated carbon-ethanol pairs suitable for cooling applications (Fig. 14).²³⁹ MOF-water-alcohol pairs were identified as strong candidates for both cooling and heating applications (Fig. 14).^{239,240} In 2021, Liu *et al.*²⁴¹ reported a screening study of 231 experimentally measured water adsorption isotherms for 6 different classes of porous adsorbents. These included MOFs, carbons, zeolites, silicic materials, composites, and other adsorbents. Isotherm data were collected from the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials.²⁴² The 231 systems were assessed according to two metrics: the coefficient of performance for cooling/heating ($\text{COP}_c/\text{COP}_h$) and the specific cooling/heating effects (SCE/SHE). Fig. 15 shows the distribution of different classes of porous materials according to their COP_c/SCE (Fig. 15a) and COP_h/SHE (Fig. 15b). Liu *et al.*²⁴¹ found that MOFs and zeolites outperform other porous adsorbents based on the $\text{COP}_c/\text{COP}_h$ and SCE/SHE metrics. The best adsorbents were found to exhibit Type V isotherms with step positions at relative pressures of 0.1–0.4 and 0–0.2 for cooling and heating applications, respectively.

Computational screening for porous materials for water adsorption remains an area ripe for development. The absence of validated interatomic potentials for adsorbent-water

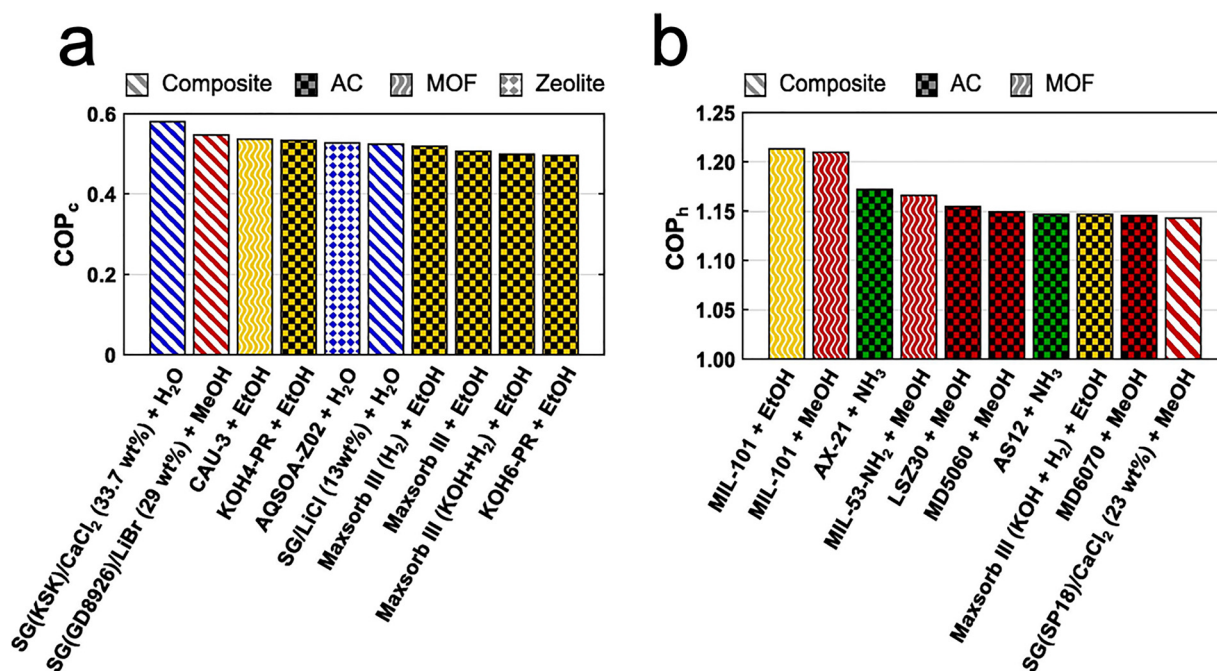


Fig. 14 Top 10 adsorbent–adsorbate working pairs for (a) cooling and (b) heating applications identified based on screening. Reproduced from ref. 239 with permission from Elsevier, copyright 2017.



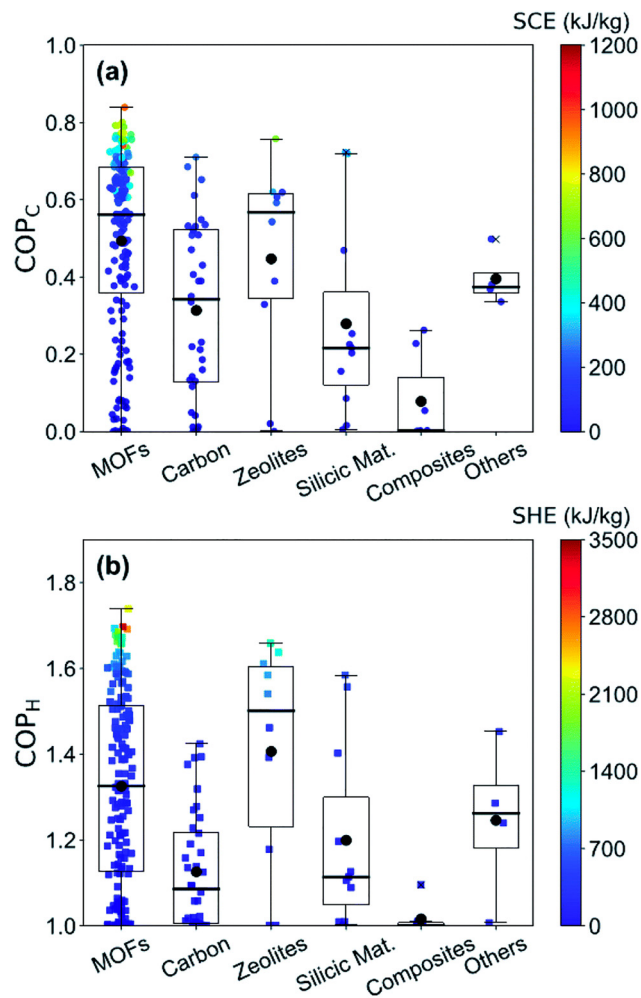


Fig. 15 Coefficients of performance (COP) for cooling (a) and heating (b) for different classes of adsorbent materials. Specific cooling/heating effects (SCE/SHE) indicate the amount of useful energy for cooling/heating, corresponding to Q_{useful} in eqn (2). COP_C and SCE were obtained at $T_{\text{evap}} = 283 \text{ K}$, $T_{\text{con}} = T_{\text{ads}} = 303 \text{ K}$, $T_{\text{des}} = 368 \text{ K}$, and COP_H and SHE were obtained at $T_{\text{ev}} = 288 \text{ K}$, $T_{\text{con}} = T_{\text{ads}} = 318 \text{ K}$, $T_{\text{des}} = 413 \text{ K}$. Reproduced from ref. 241 with permission from the Royal Society of Chemistry, copyright 2021.

interactions²⁴³ and a lack of consensus regarding atomic charges for adsorbent atoms^{244,245} have both contributed to the limited application of simulation in accelerating materials discovery. Nevertheless, significant computational advances have emerged through large-scale screening studies. High-throughput molecular dynamics investigations have evaluated over 10 000 hypothetical MOFs for thermal conductivity,

revealing that optimal performance requires material densities above 1.0 g cm^{-3} , pore sizes below 10 \AA , and four-connected metal nodes.²⁴⁶ These computational capabilities are supported by expanded databases, with the CoRE MOF Database containing over 40 000 experimentally reported structures,²⁴⁷ a nearly three-fold increase from the previous version, which contained $\sim 14\,000$ structures.²⁴⁸

Moreover, grand canonical Monte Carlo (GCMC) simulations of water adsorption in hydrophobic adsorbents are computationally challenging due to the long simulation times required to successfully sample the configuration space.²⁴⁹ The use of flat histogram sampling methods have been proposed as a potential route towards reducing simulation time.²⁵⁰ Furthermore, the hydrophilic/hydrophobic nature of porous materials reported in various databases is either unreported or unknown. To overcome this, Monte Carlo calculations of Henry's law constants (HLC) for water adsorption in MOFs have been proposed to distinguish between hydrophilic and hydrophobic MOFs.^{251,252} HLC calculations are several orders of magnitude faster than those needed to predict the adsorption isotherm.^{251,252} Despite these challenges, GCMC has been applied in a few high-throughput computational screening studies of MOFs for water adsorption, particularly in tandem with machine learning approaches for accelerating predictions.^{239,253–255}

Computational screening for porous adsorbents using alcohol as the working fluid is less challenging than for water, as intermolecular interactions involving alcohols are simpler and therefore more accurately described by interatomic potentials.²⁵⁶ Nevertheless, only a few studies on these systems have been reported.^{257–259} Li *et al.*²⁵⁸ predicted the COP_C for 1527 MOFs compiled from the CoRE 2014 database²⁶⁰ for ethanol adsorption. Guidelines were provided for selecting optimal MOF-alcohol pairs based on crystallographic (pore size and specific surface area) and thermodynamic properties (HLCs and heat of adsorption).²⁵⁸ Shi *et al.*²⁵⁹ evaluated methanol adsorption capacities of 6013 MOFs from the CoRE 2019 database²⁶¹ and 137 953 hypothetical MOFs from the Northwestern database²⁶² for heating/cooling TCES systems, including heat pumps, ice making, and refrigeration applications. They identified optimal ranges for COP working capacity, volumetric surface area (VSA), isosteric heat of adsorption (IHA), largest cavity diameter (LCD), single crystal density (ρ), and void fraction (ϕ) (Table 6). 275 COFs from the CoRE-COF 2.0 database²⁶³ were evaluated using GCMC simulations by Li *et al.*²⁶⁴ Ethanol was adopted as the working fluid and assessments were performed with respect to COP_C and COP_H . They

Table 6 Ranges of properties for MOFs from the CoRE 2019 database, *i.e.* volumetric surface area (VSA), isosteric heat of adsorption (IHA) largest cavity diameter (LCD), density, and void fraction, with a coefficient of performance (COP) and working capacity greater than the specified targets for each application. Adapted from ref. 259 with permission from the Royal Society of Chemistry, copyright 2021

| Application | COP | Working capacity (mg g^{-1}) | VSA ($\text{m}^2 \text{ cm}^{-3}$) | IHA (kJ mol^{-1}) | LCD (\AA) | Density (kg m^{-3}) | Void fraction |
|---------------|----------|---|--------------------------------------|------------------------------|----------------------|--------------------------------|---------------|
| Heat pump | > 1.75 | > 350 | 1550–3000 | 35–50 | 7.1–21.7 | 435–880 | 0.67–0.89 |
| Ice making | > 0.70 | > 170 | 1585–2947 | 34–54 | 7.1–21.7 | 434–1582 | 0.65–0.89 |
| Refrigeration | > 0.80 | > 400 | 1600–3000 | 34–52 | 7.4–20.0 | 484–1165 | 0.68–0.89 |



found that COFs are more suitable for cooling applications compared to MOFs because COFs have weaker interactions with methanol at low temperatures. Liang *et al.*²⁶⁵ calculated the adsorption and transport properties of 1072 MOFs from the CoRE MOF Database to evaluate their COP_C and SCP. The best-performing MOF exhibited a SCP of 1359 W kg⁻¹ and a COP_C of 0.64.

Design of adsorbents for TCES. Among the various categories adsorbents of interest for TCES systems, MOFs stand out due to their highly tunable properties. This tunability presents opportunities for tailoring the design of MOFs to optimize performance. For example, based on computational and experimental input, Cho *et al.*²⁶⁶ designed the MOF KMF-1, and demonstrated its promising heat storage capacity. The design involved tuning of pore channels and hydrophilicity by selecting and functionalizing the 2,5-pyrroledicarboxylate (PyDC) linker. These design choices were informed by analyzing the structure and performance of two well-known MOFs:²⁶⁷ CAU-10 and MIL-160. Similarly, Rieth *et al.*²⁶⁸ designed two isoreticular triazolate MOFs with record-setting values for COP (1.63). They demonstrated how to control the relative humidity at which water uptake occurs by modulating the pore size. Finally, Rieth *et al.*,²⁶⁹ demonstrated an increase in the reversible water uptake of two MOFs (Ni₂Cl₂BTDD & Ni₂Br₂BTDD, where BTDD = bis(1,2,3-triazolo-[4,5-*b*],[4',5'-*i*])dibenzo-[1,4]-dioxin) by systematic anion exchange. Recent work has also demonstrated the use of mixed-linker MOFs for TCES, enabling tuning of hydrophilicity and volumetric energy density. A notable example is KMF-2, a mixed-linker Al-MOF incorporating isophthalate and pyridinedicarboxylate linkers, which exhibits a COP for cooling of 0.75 with a volumetric heat capacity of ~330 kWh m⁻³ at regeneration temperatures < 70 °C.²²⁰

Techno-economic analysis of adsorbents. Shi *et al.*²⁵⁹ conducted a techno-economic analysis of real and hypothetical MOFs for use in adsorption heat pumps/chillers with methanol as the working fluid. Their analysis considered the equipment cost, cycle cost, and materials cost. The materials cost was identified as the most significant. They identified 12 MOFs with a low system-level cost of ~1 USD per kJ in heat-pump/chiller applications. Shi *et al.* validated their analysis by synthesizing a variant of Cu₃BTC₂,²⁷⁰ measuring its methanol capacity and estimating costs. Emerging techno-economic analyses for porous adsorbents now consider life-cycle emissions, regeneration energy requirements, and material scalability. While most existing models focus on general adsorbents, similar scoring frameworks are being adapted to MOFs and COFs for solar-driven TCES applications.²⁷¹

Characterization and system integration of porous adsorbents. Water adsorption/desorption characterization at multiple temperatures enables the optimization of working capacity and COP for heat pump applications, with experimental studies demonstrating that MOFs like MIL-100(Fe) achieve COP values of 0.80 and specific cooling of 569.42 kJ kg⁻¹.²⁷² Thermal cycling stability measurements reveal that zeolite-based

composites maintain performance over hundreds of cycles, with zeolite 13X/MgCl₂ systems showing heat storage capacities of 686.86 kJ kg⁻¹.²⁷³ System integration approaches address thermal transport limitations of porous materials through composite design. For example, zeolite-graphene nanoplatelet composites demonstrate thermal conductivity improvements up to 127 times over pure zeolite while maintaining 43% improvement in volumetric water uptake.²⁷⁴ These approaches leverage the high energy density of porous adsorbents while incorporating enhanced heat transfer capabilities needed for practical applications.²⁷⁵

Commercial deployment and market outlook for porous adsorbents. Zeolite–water systems have achieved commercial deployment in residential applications, with demonstrated energy densities of 150–200 kWh m⁻³ and capabilities for seasonal heat storage with limited heat loss.²⁷⁶ Pilot-scale demonstrations include household-scale systems with 250 L zeolite-based system achieving storage capacities of 52 kWh and maximum delivered power of 4.4 kW.²⁷⁷ MOF-based systems continue to be researched, with MOF-ammonia working pairs showing promise due to their performance under extreme climates compared to conventional sorbent-ammonia pairs.²⁷⁸ Improvements for industrial heat pumps have been demonstrated in MOF-water systems like aluminum fumarate, which can operate at desorption temperatures as low as 65 °C.²⁷⁹

D. Class III: sorption in liquids

Liquid sorptive TCES operates by reversibly concentrating and diluting a solute (*e.g.* LiBr) by exchanging the solvent (*e.g.* H₂O) between vapor and liquid phases.^{280–283} Spontaneous absorption of the vapor into the liquid solution releases heat, while solute desorption/vaporization is the mechanism by which heat is stored. The solute–solvent and solvent–solvent binding interactions are primarily van der Waals in nature; they can be supplemented by hydrogen bonding for solvents such as water, alcohols, and ammonia. In the solution, the chemical potential of the solvent is reduced due to interactions with the solute. According to the Gibbs–Duhem equations, the chemical potential μ of the solvent (*e.g.* water) decreases as the concentration of the solute increases. Thus, the vapor pressure over water solutions is lower than that for pure water:²⁸⁴

$$\mu(T) = \mu^0(T) + RT \ln a = \mu^0(T) + RT \ln \frac{P}{P^0} \quad (23)$$

$$\mu(T) = \mu^0(T) + RT \ln \frac{RH}{100\%} \quad (24)$$

where standard state refers to pure water, a is water activity ($a = 1$ for pure solvent), P^0 is saturated vapor pressure at temperature T , and RH is the relative humidity at temperature T for the case of water. The activity of salts in water solutions may be estimated from Debye–Hückel theory at low ionic strength of solution on the order of 10⁻³ M. For higher concentrations, including brines, semi-empirical models such as the Pitzer–Simonson–Clegg model can succeed in predicting the activity of water.²⁸² However, the availability of parameters



for such models remain limited mainly due to their experimental origin, which makes the targeted design of solutions for absorptive applications challenging.

While there is no general theory for calculating activities for very high concentration solutions used for sorptive applications, qualitative considerations for ionic salts suggest that a higher dissolution enthalpy and a lower activity for water is observed for the case of hard ions (more polarizing, smaller radii) that form crystallohydrates with low lattice energy. The activity of water in saturated solutions corresponds to the deliquescence relative humidity and can be found in the literature.¹²⁷

A typical P-T phase diagram for salt-H₂O systems (Fig. 16) consists of the solution region, the region corresponding to the highest hydrate Salt·nH₂O, and the area of the lower hydrates and/or the anhydrous salt. Accordingly, there are three types of sorptive cycles with various technical implementations, namely, cycles with only absorption/desorption within a (liquid) solution (cycle identified with green lines in Fig. 16), cycles involving crystallization of the highest hydrate (blue cycle) and cycles involving decomposition of the highest hydrate into lower hydrates and/or the anhydrous salt (red). Below, the energy storage densities and temperature lifts for the most popular working pairs for all three cycle types are described.

Absorption and crystallization cycles. Absorptive heat storage or cooling cycles typically consist of two isobars corresponding to sorption/desorption and two isosteres corresponding to strong (concentrated) and weak (diluted) solutions. The energy storage density ESD_{ab} on the materials level can be calculated from the enthalpy difference between strong and weak solutions, or from the specific absorption enthalpy:

$$ESD_{ab} = \frac{1}{V_M} \int_{c_s}^{c_w} \overline{\Delta_{ab}H}(c) dc \quad (25)$$

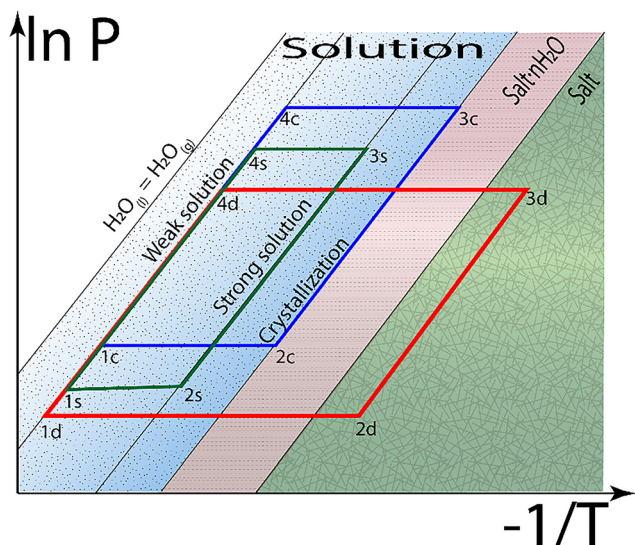


Fig. 16 Generic phase diagram for a water-salt system in van 't Hoff coordinates illustrating three types of absorptive heat storage cycles: (green) sorption in a liquid phase, 1s-2s-3s-4s; (blue) three-phase storage, 1c-2c-3c-4c; (red) storage with full decomposition, 1d-2d-3d-4d.

where c_s and c_w are concentrations of the strong and weak solution, and V_M is the molar volume of weak solution.

Due to low temperatures and concentration span, systems based on liquid sorption have relatively low temperature lift. For domestic heating, the most popular solutes are NaOH, KOH, CaCl₂, LiBr, HCOOK, glycerol and ammonia.^{60,62} For cooling applications, non-water solvents are preferred, and the list is supplemented by alcohol-based pairs such as LiBr-CH₃OH and LiBr-C₂H₅OH.^{285,286} Ionic liquids represent a novel alternative for which crystallization is not reached.^{287,288}

A trade-off between energy storage density and temperature lift exists for absorptive cycles: higher energy storage densities are achieved at the expense of lower temperature lift, and *vice versa*. This approach to absorptive storage allows for low charging temperatures (<80 °C); the largest energy storage densities for heat storage in buildings may reach 1 GJ m⁻³ (Table 7), however the temperature lift is modest, 10–15 °C. The temperature lift can be boosted by increasing the charging temperature to access the crystalline hydrate, thus allowing access to the crystallization energy ESD_{cr}. One drawback of this approach is that the complexity of the system design must increase to account for these ‘three-phase cycles’ that permit melting and solidification/crystallization of the storage medium. Three-phase thermal energy storage systems have been commercialized by ClimateWell.

Decomposition cycles. A further increase of energy storage density (compared to a three-phase cycle with crystallization) can be achieved by increasing the charging temperature to dehydrate the crystalline salt (red cycle in Fig. 16). In this case the energy storage density is given by:

$$ESD_d = ESD_{cr} + ESD_{ab} + \frac{1}{V_M} \Delta_{dec} H^0 \quad (26)$$

where $\Delta_{dec} H^0$ is the specific decomposition enthalpy for the transition (or series of transitions) associated with the lower hydrates and/or complete dehydration. The most promising materials for thermal energy storage in this usage mode involve salts capable of forming hydrates with appropriate DRH = 10–40% such as LiCl, CaCl₂, MgCl₂, MgSO₄, K₂CO₃ (Table 8).

The practical realization of these decomposition cycles is difficult without the aid of porous media that provide efficient heat/mass transfer within the sorbent bed during cycling.²⁸⁹ While such composites should allow high charging

Table 7 Salt-solvent working pairs for heating and cooling absorptive cycles and their characteristics. ‘Crystallization’ indicates whether the solvates are crystalline

| Working pair | Crystallization | $T_{evap}/T_{release}/T_{storage}$ (°C) | ESD _{ab} , GJ m ⁻³ | Ref. |
|---------------------------------------|-----------------|---|--|------|
| LiBr-H ₂ O | No | 7/43/80 | 0.40 | 350 |
| LiBr-H ₂ O | Yes | 10/20/93 | 1.4 | 111 |
| CaCl ₂ -H ₂ O | No | 10/20/45 | 0.43 | 351 |
| CaCl ₂ -H ₂ O | Yes | 10/20/54 | 0.95 | 111 |
| LiCl-H ₂ O | Yes | 10/20/66 | 1.4 | 111 |
| LiBr-CH ₃ OH | Yes | 5/35/75 | 0.2 | 352 |
| LiCl-CH ₃ OH | Yes | 10/35/75 | 0.8 | 352 |
| LiBr-C ₂ H ₅ OH | Yes | 10/30/95 | 0.2 | 353 |



Table 8 Examples of “Salt in porous matrix” composites, with their corresponding specific energy, ESD per unit bed volume, $T_{\text{evap}}/T_{\text{release}}$ for the heating cycle, and exergy storage density (ExSD)

| Salt | Matrix | Specific energy (MJ kg ⁻¹) | ESD (GJ m ⁻³) | $T_{\text{evap}}/T_{\text{release}}$ (°C) | ExSD (MJ m ⁻³) | Ref. |
|--------------------------------|-----------------------------------|--|---------------------------|---|----------------------------|------|
| CaCl ₂ | Hollow silica | 1.1 | 0.86 | 13/45 | 96 | 49 |
| CaCl ₂ | Ethylcellulose | 2.1 | 0.4 | 10/20 | 14 | 354 |
| CaCl ₂ | SiO ₂ (Grace Davisil™) | 1.1 | 0.76 | 10/30 | 54 | 355 |
| CaCl ₂ | Silica-alumina | 0.9 | 0.65 | 3/20 | 40 | 356 |
| CaCl ₂ | PHTS ^a | 1.2 | — | 10/30 | — | 357 |
| CaCl ₂ | MIL-101(Cr) | 1.6 | 1.0 | 10/30 | 71 | 358 |
| LiCl | UiO-66 | 0.9 | — | 10/40 | — | 291 |
| LiCl | Hollow silica | 0.75 | 0.65 | 13/45 | 73 | 49 |
| LiCl | Hollow silica | 0.63 | 0.52 | 13/60 | 85 | 49 |
| LiCl | MWCNT + PVA ^b | 1.6 | 0.65 | 10/35 | 57 | 359 |
| LiCl | Expanded vermiculite | > 1.8 | 0.8 | 10/35 | 70 | 360 |
| LiCl | SiO ₂ (Fuji Type A) | 1.1 | 0.6 | 15/40 | 52 | 361 |
| MgCl ₂ | Zeolite 13x | 1.2 | — | 25/62 | — | 362 |
| SrBr ₂ | Hollow silica | 0.69 | 0.63 | 18/45 | 59 | 49 |
| SrBr ₂ | Expanded vermiculite | 1.6 | 0.38 | 20/30 | 13 | 339 |
| SrBr ₂ | MIL-101(Cr) | 1.35 | 0.84 | 10/30 | 59 | 363 |
| K ₂ CO ₃ | Expanded vermiculite | — | 0.9 | 20/30 | 31 | 344 |

^a Plugged hexagonal templated silicate. ^b MultiWall Carbon NanoTubes with polyvinyl alcohol binder.

temperatures and high relative volume change of the active storage component, the skeletal volume of the porous matrix and void space in pores necessary to accommodate for the resultant solution (to avoid leakage) decreases the effective energy storage density of the composite relative to that of the pure salt (Table 8). For this reason, the most popular porous matrices are formed from mechanically stable particles with large porosity and sub-micrometer pores capable of containing the salt solution *via* capillary forces. Popular and inexpensive options include vermiculite, attapulgite, and silica gel.²⁹⁰ Recently, MOFs are being considered as promising matrices due to their high porosity, which yields a potentially high fraction of “useful” space to be occupied by a salt.^{291–293} Finding a balance between energy storage density on the bed level, temperature lift, and heat/mass transfer is one important remaining challenge.⁴⁹

Suggested directions for future research

The preceding sections have introduced the primary classes of materials for low-temperature thermochemical storage and summarized their respective attributes and performance limitations. Based on those limitations, this section suggests high-priority research directions aimed at overcoming performance gaps and accelerating the adoption of TCES devices.

Computational materials discovery

A comprehensive materials discovery effort has not been performed in the field of thermal energy storage. The absence of such an effort differs from that of related applications – *e.g.*, electrochemical energy storage, photovoltaics, CO₂ capture, *etc.* – in which the properties of an active material largely determine the performance of its respective device. Recent materials discovery efforts targeting these other applications have taken advantage of accurate and efficient computational methods coupled to high-performance computing.^{294–305} These

efforts have demonstrated the capability to screen large databases of materials containing as many as 10⁶ distinct compositions.^{306–308}

Two of the most widely used computational methods for materials discovery are Density Functional Theory (DFT) and classical Grand Canonical Monte Carlo (GCMC). Although both techniques simulate matter at the atomic scale, they differ in their approach to describing atomic interactions (*i.e.*, bonding) and therefore exhibit distinct capabilities with respect to the size of systems that can be simulated and the properties that can be predicted. DFT is a quantum-mechanical technique that solves for the ground state electron density and total energy of a material. These quantities allow for the accurate prediction of energy densities and other macroscopic thermodynamic quantities such as enthalpies and free energies, both of which are relevant for predicting the equilibrium properties of TCES materials, such as the turning temperature.³⁰⁹ The high accuracy of DFT calculations comes at the cost of high computational expense: if the goal is to screen thousands of compounds in a reasonable time-frame (several months), then the size of the simulation cells generally cannot exceed ~100 atoms. Fortunately, this size limitation allows calculations on a sizeable sub-set of the materials classes of interest to TCES, such as salt hydrates.^{87,203,205}

In contrast to DFT, classical GCMC can simulate large systems. This feature makes it useful for simulating adsorption in porous hosts, such as MOFs and zeolites, where the simulation cell ranges from hundreds to thousands of atoms.^{249,255,310–312} The greater computational efficiency of classical GCMC reflects its use of a predefined interatomic potential, which can be evaluated with low computational cost. GCMC is a statistical sampling method that predicts equilibrium properties within the grand canonical (μ VT) ensemble.³¹³ In the context of an adsorption process, the simulation consists of a fictitious gas reservoir at constant chemical potential, $\mu(P,T)$, and a porous host into which the



gas molecules may adsorb. The output of the simulation is the equilibrium number of molecules adsorbed within the host at the prescribed chemical potential of the gas (which corresponds to a constant pressure and temperature). An adsorption isotherm can be predicted by calculating the number of molecules adsorbed as a function of pressure at constant temperature.³¹³ The adsorption enthalpy can also be calculated from such simulations.³¹⁴ As adsorption isotherms and enthalpies are also routinely measured experimentally,^{315,316} a direct comparison between theory and experiment is possible.

The primary shortcoming of classical GCMC derives from inaccuracies in the interatomic potential. If the potential does not accurately capture the nature and strength of bonding, then the quantities derived from it – uptake capacity, shape of the isotherm – will reflect these inaccuracies.³¹¹ These inaccuracies arise partly from the fact that most classical GCMC simulations assume a rigid H₂O geometry. In reality, however, the H–O–H bond angle and O–H bond lengths of water molecules depend on their local environment within the MOF, which can affect the nature of their interatomic interactions.²⁴⁹ This effect is neglected.

At present, DFT and GCMC screening have been applied only to a limited set of potential TCES materials. This includes known salt hydrates, hypothetical salt-hydrates based on halogen anions, and a small number of studies on adsorption in porous materials.^{87,203,205,249,250,259,317} The largest study to date is that of Shi *et al.*,²⁵⁹ who examined methanol adsorption in more than 140 000 real and hypothetical MOFs. An even larger space exists for hydrates of ‘mixed metal’ salts, where the cation sites are occupied by two or more distinct cations. In all these cases computation can be used to assess the thermodynamic stability of various hypothetical hydrate compositions, predict capacities, and estimate equilibrium turning temperatures. Subsequently, experiments should be performed to validate the synthesizability and performance of the most promising materials.

Similar discovery opportunities exist for adsorption in porous hosts. Here, the most promise arguably lies with MOFs. This promise reflects the compositional and structural tunability of MOFs – approximately a million MOF variants have been proposed^{318–321} – but is also inspired by their crystallinity: the regularity of the pore structure in MOFs implies low tortuosity for mass transport, potentially enhancing the power density of a MOF-based thermal storage device. As with absorption in salts, care must be taken in the screening to assess stability of any new MOF composition. This is especially important in the case where water is the adsorbate, as some MOFs will undergo (irreversible) hydrolysis in humid environments.¹⁰⁷ For this reason, extending the screening to adsorbates other than water is an area also worth exploring.

Enhancing power density. As discussed in the preceding sections, a practical thermal storage device must store and release heat at rates that are fast enough to meet the requirements of the desired application. In turn, this system-level requirement places constraints on the underlying properties of the storage material(s), such as their thermal conductivity. In the case of TCES materials, where a chemical reaction is responsible for the uptake/release of heat, several factors

beyond thermal conductivity contribute to the achievable power density. These include intrinsic kinetic phenomena within the active storage material and larger-scale microstructural features that influence long-range heat and mass transport.^{131,140,322}

Regarding the intrinsic kinetics of the storage material, let us consider the discharge of a salt-hydrate-based TCES device. During discharge, the anhydrous salt and water vapor react to form a salt-hydrate through absorption of the water into the solid salt. As the salt-hydrate is a distinct crystalline phase, the rate of its formation (and the accompanying rate of heat release) is governed by nucleation and growth processes, either of which may be rate-limiting.³²³ The rate of nucleation of the hydrate is governed by a nucleation energy barrier associated with the formation of nanoscopic nuclei of the nascent hydrate phase.⁵⁷ Subsequent growth of these nuclei requires rearrangement of the salt’s crystalline lattice to adopt the new structure of the hydrate, and transport of water to the salt/hydrate two-phase interface.¹³¹ To achieve high power density, one must ensure that both of these processes are sufficiently fast.

Similar kinetic limitations exist in hydrogen storage materials. Known strategies from the hydrogen literature for overcoming these limitations may be relevant to TCES materials that operate *via* absorption and should be investigated. One important strategy is doping. Bogdanovic *et al.*³²⁴ were the first to demonstrate that doping sodium alanate, NaAlH₄, with titanium significantly enhances the hydrogenation kinetics. This effect has been reported in other complex hydrides and with other dopants.^{323,325–328} Although the exact mechanism responsible for the kinetic enhancements remains a matter of debate, it is reasonable to hypothesize that similar beneficial effects may be realized for absorption reactions of interest for TCES. Some progress in this regard has already been achieved.^{149,327}

The second strategy that could be adopted from the field of hydrogen storage is impregnation of the active TCES material within a porous host. This approach has been used to improve the kinetics of complex hydrides,^{329–331} and in some cases have resulted in dramatic changes to reaction behavior.^{332,333} These improvements are hypothesized to result from reductions in particle size (which is constrained by the pore diameter) and associated diffusion lengths, and by phenomena associated with the guest/host interface. The downside to this approach is that the mass and volume of the (inactive) host decreases the system’s specific energy and ESD.

Finally, we note that the limitations associated with nucleation and growth during absorption in solids are much less severe in materials that operate *via* adsorption.^{334–336} This behaviour provides further motivation for developing materials such as MOFs for TCES. In the field of hydrogen storage, the kinetic performance of MOFs is well-known to surpass that of materials that operate *via* absorption, such as complex hydrides.^{337,338}

Conclusions

Heat is a primary component of the world’s energy ecosystem. Its prevalence implies that its use and manipulation have major



implications for energy efficiency and carbon emissions. The development of systems that can store and manage heat would have a positive impact upon numerous processes throughout multiple sectors of the global economy.

This review has focused on the materials that underlie systems that store and manipulate heat, with an emphasis on those that operate *via* thermochemical reactions. Starting from an overview of general concepts, a detailed discussion of properties relevant for low-temperature (domestic) applications is subsequently presented. These applications include domestic heat storage/amplification (hot water heating), adsorptive cooling (air conditioning), and heat-moisture recuperation. Although these systems remain in an early stage of development, their commercialization will be accelerated by improving the performance of their respective thermal storage materials. This goal motivates a deep-dive into three main classes of low-temperature thermochemical storage materials: (i) absorption in solids (hydrates, ammoniates, and methanolates); (ii) sorption in porous hosts (metal-organic frameworks); and (iii) dilution in liquids. For each class the underlying storage mechanisms are introduced, benchmark materials are discussed, and a summary of advantages and limitations is provided. Although not widely discussed, the implementation of thermal energy storage also needs to consider the potential limited availability of raw materials and production constraints.

Finally, opportunities are described for research aimed at developing optimal thermochemical energy storage materials. Discovery of new storage materials and the development of strategies for increasing the rate of the heat-storing reaction – thus improving power density – are proposed as two important areas that are ripe for research and development.

Author contributions

All authors made significant contributions to the drafting of this review.

Conflicts of interest

There are no conflicts to declare.

List of abbreviations

| | |
|--------|---|
| ARPA-E | Advanced Research Projects Agency - Energy |
| BTU | British thermal units |
| CAU | Christian-Albrechts-Universität |
| CNT | Carbon nanotube |
| COP | Coefficient of performance |
| CoRE | Computation-ready, experimental |
| DFT | Density functional theory |
| DOE | Department of Energy |
| DRH | Deliquescence relative humidity |
| ESD | Energy storage density |
| ETIP | European technology and innovation platform |
| EU | European Union |

| | |
|-------|---|
| GCMC | Grand Canonical Monte Carlo |
| GJ | Giga-Joules |
| HLC | Henry's Law Constant |
| HTF | Heat transfer fluid |
| HVAC | Heating, ventilation, and air conditioning |
| ICSD | Inorganic crystal structure database |
| IHA | Isosteric heat of adsorption |
| IUPAC | International Union of Pure and Applied Chemistry |
| LCD | Largest cavity diameter |
| LD50 | Lethal Dose 50 |
| MIL | Materials of Institute Lavoisier |
| MJ | Mega-Joules |
| MOF | Metal-organic framework |
| NIST | National Institute of Standards and Technology |
| PCM | Phase change material |
| PV | Photovoltaic |
| RH | Relative humidity |
| RHC | Renewable heating and cooling |
| SCE | Specific cooling effect |
| SCP | Specific cooling power |
| SHE | Specific heating effect |
| TCES | Thermochemical energy storage |
| TES | Thermal energy storage |
| VSA | Volumetric surface area |

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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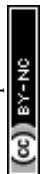
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