

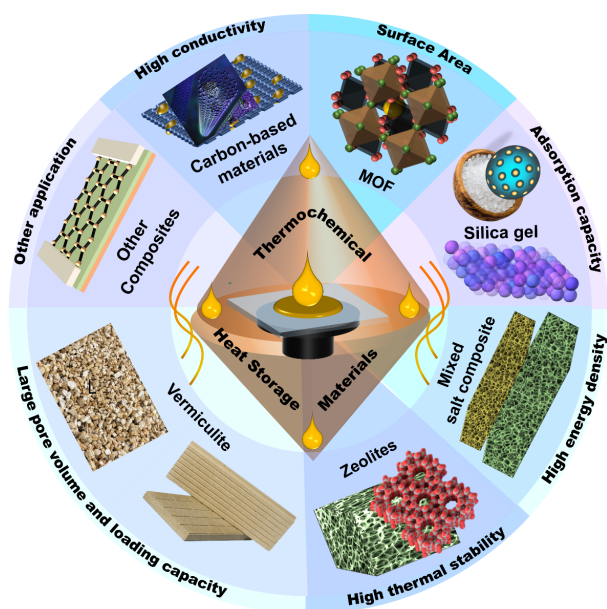
Graphical Abstract

Synergistic salt hydrates and advanced porous matrix composites for high-performance thermochemical heat storage: A review

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This review highlights how salt hydrates integrated with advanced porous matrices such as metal–organic frameworks (MOFs), zeolites, silica gel, carbon-based materials, and mineral frameworks overcome key limitations in thermochemical heat storage, including agglomeration, deliquescence, low thermal conductivity, and slow sorption kinetics. Confining hygroscopic salts within conductive, porous hosts enhances heat and mass transfer, cyclic stability, and energy storage density. This review also highlights the promise of binary-salt and hybrid porous composites for use in next-generation, high-performance, sustainable heat storage systems.

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Synergistic salt hydrates and advanced porous matrix composites for high-performance thermochemical heat storage: A review

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ABSTRACT

Thermochemical heat storage (TCHS) is a technology that stores thermal energy through reversible chemical reactions, providing high energy density and long-term storage with minimal losses. This review highlights recent advancements in the use of salt hydrates and porous matrix composites as sorbents in TCHS systems, with a focus on their synergistic effects. It begins with an overview of heat storage systems and adsorption concepts. This discussion then addresses key challenges related to salt-hydrated and composite adsorbent materials. In practical applications, salt hydrates for thermochemical heat storage face issues such as deliquescence, agglomeration, poor kinetics, and low thermal conductivity. Consequently, this review systematically categorizes hygroscopic salts embedded in porous host matrices, including zeolite-based materials, silica gel, carbon-based composites, minerals, metal–organic frameworks (MOFs), and mixed-salt composites. These findings highlight that high-conductivity carbon-based materials are utilized to enhance heat transfer, and that MOFs and zeolite 13X can improve sorption performance. Composite materials are analyzed to prevent agglomeration, enhance cyclic efficiency, and increase energy density. Additionally, binary salts confined within porous matrices exhibit notable synergistic effects on overall performance. Finally, the review discusses current limitations and suggests future research directions for developing suitable material–adsorbate pairs.

KEYWORDS

thermochemical heat storage, sorption, composite materials, energy density

1 Introduction

Global climate change requires greater use of renewable and sustainable energy to reduce the reliance on fossil fuels and lower CO₂ emissions, which drive the greenhouse effect. Energy is a primary requirement for humanity and plays a key role in all countries^[1]. Fossil fuels remain the predominant energy source in China despite their substantial contributions to environmental pollution and climate change^[2]. To address climate change, the government has set targets to peak carbon emissions by 2030 and achieve carbon neutrality by 2060^[3]. As a result, the share of renewable energy for building heating is expected to grow rapidly. A key challenge with renewable energy, such as solar energy, is the supply–demand mismatch caused by its intermittent nature^[4–6]. Bridging the gap between energy supply and demand remains a challenge^[4]. Consequently, the efficient utilization, transformation, and storage of energy are essential components of environmentally friendly and sustainable development. Thermal energy storage (TES) technologies are emerging as promising solutions to meet these challenges because of their high

energy density, high conversion efficiency, and low application costs. TES technology provides a means to store thermal energy from various sources, including renewable and nonrenewable sources, independent of demand; consequently, temporarily available energy is transformed into permanently accessible energy^[7].

The upward trajectory in publications over recent decades reflects a marked increase in research and development focused on thermochemical energy storage (TCES). To quantify this trend, a systematic search of the Web of Science database was conducted for international papers published between 2016–2025 using the keyword “TCES”. The proliferation of peer-reviewed literature on TCES technology in recent years is evidenced by a concomitant increase in both the number of publications and the frequency of citations (Fig. 1).

A key advantage of TES systems is their ability to store thermal energy over an exceptionally wide temperature range, from subzero temperatures to temperatures greater than 2000°C (Fig. 2a)^[8,9]. In TES systems, heat is transferred from one medium, the heat transfer fluid (HTF), to another and to an energy storage substance. The charging

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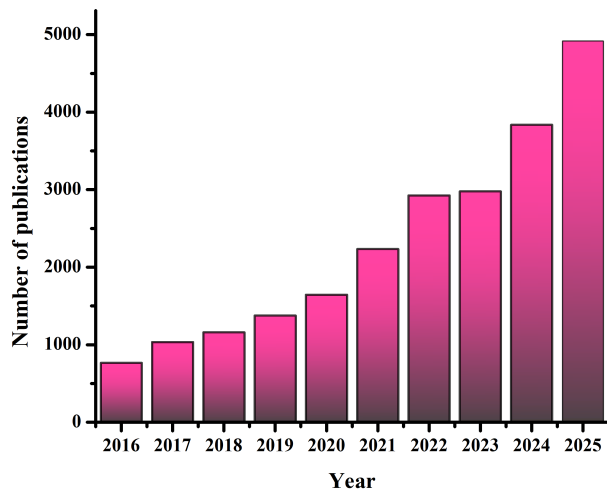


Figure 1 Total number of global TCES-related publications.

process increases the temperature of the energy storage material, and the resulting thermal energy is transferred to the HTF, where it is used for a particular purpose. With respect to charging, concentrated solar energy or another sustainable energy source works well. Heat storage types

are classified into three primary forms: thermochemical heat storage (TCHS), latent heat storage (LHS), and sensible heat storage (SHS). SHS, which involves heating or cooling a liquid or solid storage medium without changing its phase, is the best-known heat storage technique. The storage capacity is directly proportional to the temperature change and is determined by the specific heat capacity of the material. To achieve a high energy storage density (ESD), the materials should be dense and have a high specific heat capacity. This enables storage tanks to be built more simply and compactly. In accordance with the above idea, the use of a large heat-storage device is a major drawback of a low ESD^[10].

As a result, inexpensive energy storage materials such as LHS are readily available. In the LHS system, the energy storage material undergoes a phase transition, usually from solid to liquid. During discharge, the substance solidifies and releases energy as latent heat (specifically, the heat of fusion during melting/freezing). Because phase change materials (PCMs) have a broad range of melting temperatures, the energy they release can be tailored to specific applications. PCMs enable compact, effective TES by storing and releasing significant amounts of latent heat during phase transitions. They use less material than SHS

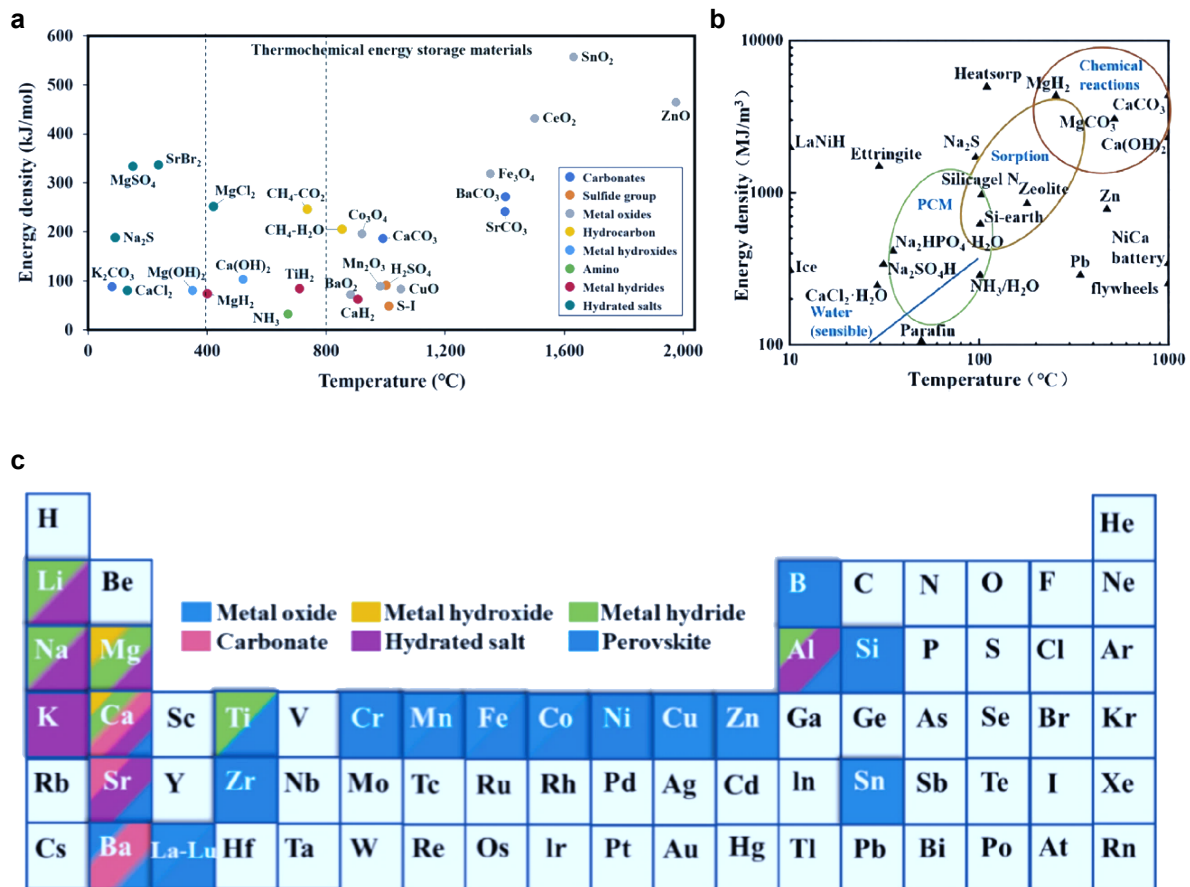


Figure 2 Characterization of TCHS materials and their applications: (a) Material classification by operating temperature salt hydrates for low-temperature building use (<200°C), hydroxides and carbonates for medium-temperature industrial processes (200–500°C), and redox metal oxides for high-temperature solar power (>500°C). (b) Higher energy density of thermochemical storage compared with sensible and latent methods across all temperature ranges because of chemical bond formation rather than thermal gradients. (c) Essential metallic elements (Mg, Ca, Sr, K, Al, etc.) enabling reversible thermochemical reactions. Reproduced with permission from Ref. [8] ©2025, Elsevier Ltd.

systems do because of their high energy density, thereby reducing weight and space requirements. In contrast to SHS materials, PCMs absorb and release heat at nearly constant temperatures, which ensures stable thermal management. The drawbacks include high cost, toxicity, and hygroscopicity (or possibly deliquescence). Moreover, the low thermal conductivity and phase separation of PCMs limit their use^[11,12]. As large-scale new energy systems are developed and deployed, the limitations of conventional storage methods become apparent. In this context, compared with sensible and latent heat systems, TCHS has emerged as a promising alternative, offering a higher heat storage density. TCHS is a technique that uses a binary working pair to store heat energy on the basis of chemical or physical bonding. A sorbent and an adsorbate are the two components of this process; the adsorbate is always a gas or water vapor, while the sorbent can be either a liquid or a solid. The nature of the interaction between the sorbent and the sorbate categorizes TCHS systems. These systems can be broadly divided into sorption-based and chemical reaction-based storage systems. Sorption-based methods are further delineated into two distinct subtypes: physisorption, governed by weak van der Waals forces, and chemisorption, which involves the formation of stronger chemical bonds. In a reversible sorption process or chemical reaction, the released heat is stored separately and is referred to as the charging (heat storage) and reverse discharging (heat release) phases, with the degree of reaction (physical sorption or chemical reaction) determining the extent of heat storage. Thermochemical reactions are reversible processes that, depending on whether they are endothermic or exothermic, either absorb or release heat. Discharging is an exothermic process, whereas charging is an endothermic reaction. Owing to its simplicity, a single-stage absorption TCHS device has been employed by several researchers. Additionally, a prototype was created for use, such as heat transformation, space heating, cooling, and household hot water delivery^[13–15].

In a chemical reaction-based TES device, the heat released during the reverse reaction (exothermic) forms new bonds between the components, while the energy required to break bonds (endothermic) is stored separately and released when heat is needed. During chemisorption hydration, water molecules become chemically integrated into the crystal lattice of the anhydrous salt. The main difference between chemisorption and physisorption lies in the type of bonding. In chemisorption, strong, typically irreversible chemical bonds form between the sorbent and the sorbate, whereas in physisorption, weak van der Waals forces cause the sorbate to adhere to the sorbent reversibly^[16]. The two main benefits of a TCHS system are high ESD and long-term energy storage with little loss (Fig. 2b). These benefits have attracted researchers' attention. TCES has fewer publications than other TES systems do, according to a research study by Spietz et al.^[9]. A geographic analysis of this body of work reveals that China, the United States, and Germany have undertaken the most substantial research efforts, collectively shaping the current state of the art^[17]. Despite the growing interest in TCES systems, only a limited number of studies have systematically classi-

fied and evaluated the properties of host matrices for salt hydrates, particularly their role in enhancing the energy storage performance of the resulting composites. While previous studies have summarized primarily advancements in TCES devices and salt hydrates, often with an overview of prevailing challenges, the present review adopts a more focused scope. Its central aim is to provide a systematic examination of three key material classes for TCHS: salt hydrate-based materials, salt-hydrate porous matrix composites, and binary salt composites. For each category, the review offers a critical overview of its fundamental characteristics, inherent drawbacks, and synergistic interactions between host matrices and embedded salts.

Subsequently, the intricate relationships among salt concentration, adsorption capacity, and ESD are discussed. Particular emphasis is placed on elucidating how the host matrix's structural morphology and thermal conductivity govern the reaction kinetics and overall thermal behavior of the composite materials. By synthesizing these insights, the review organizes the fragmented body of literature into a coherent and accessible framework, offering a roadmap for future material development and performance optimization. The review concludes with a set of targeted recommendations to guide subsequent research in this rapidly evolving field.

2 Thermochemical heat storage materials

The overall efficiency of the TCES system is influenced by the thermochemical properties of thermochemical materials (TCMs). The qualities of TCMs, in particular, are essential to an energy storage system. A chemical compound capable of storing heat is the fundamental component of a heat-storage material. Through phase transitions, heat-storage materials absorb heat from their surroundings and release energy as needed. As a result, heat-storing materials can effectively modify the surrounding environment temperature and improve energy efficiency. The heat storage phase and the heat release phase are the two stages of the heat storage material. At this point, the excess energy, industrial byproduct heat, or solar electricity during periods of high demand are captured by the heat storage material. The stage of heat emission occurs next. The TES material will now release heat for daily activities and production^[18]. Heat storage materials can reduce fluctuations in heat energy over time and space, enabling efficient energy use and conservation. The stages of heat storage and release alternate^[19,20].

Small-sized particles have high surface area-to-volume ratios and accelerated heat transfer rates^[15]. TCHS materials encompass a broad range of chemical components, including metal oxides, metal hydroxides, metal hydrides, carbonates, sulfur-based compounds, hydrocarbons, ammonia, and hydrated salts, as illustrated in Fig. 2c^[8]. Through thermochemical processes, these material groups provide distinct qualities and capabilities for energy storage and release^[8]. Consequently, hydrated salts have emerged as particularly promising candidates for TCES materials owing to their advantageous properties, favorable performance metrics, and demonstrated applicability across various TCES technologies. TCMs constitute the core component of such systems^[4]. Given that sorbents function as solid sorbents that interact with vapor-phase

sorbates, identifying optimal candidates is paramount to the development of efficient and sustainable TCES solutions. Accordingly, the present study seeks to evaluate and identify the most promising hydrated salt-based materials. To guide this assessment, an ideal TCM should exhibit the following characteristics, as outlined in the literature^[19,21,22]:

- High energy density (gravimetric and volumetric) and significant sorption capability;
- Low charging temperature, effective heat and mass transfer, and strong thermal stability;
- Harmless, noncorrosive, nontoxic, and environmentally protective effects with minimal global warming and ozone depletion impact;
- Good mechanical strength and excellent thermal/molecular stability under specified operating conditions;
- High thermal conductivity and significant heat transfer with heat transfer fluid during adsorption;
- Minimized desorption temperature, appropriate permeability, and reduced recovery temperature (for high solar fractions);
- Low cost and nonhazardous.

No single sorbent or TCM can simultaneously satisfy all of the aforementioned requirements; nevertheless, these factors must be carefully balanced to achieve optimal overall performance. Commonly known problems with anhydrous salts for TCHS include poor thermal conductivity during heat transfer during hydration/dehydration, poor cyclic efficiency (a tendency to lose energy after some operating cycles), degradation due to continuous swelling during adsorbate uptake and cracking, and changes in porous structure. The others are low-energy-density and low-kinetic-energy reactions. The energy density of hydration depends on the type of salt selected, which has a specific reaction energy, the amount of adsorbate, and reaction conditions such as the humidity ratio and temperature^[23–25]. Currently, the focus is on developing a TCHS as a route to new composite materials that meet the requirements for high energy density and cyclic performance.

3 Single-salt hydrates for thermochemical heat storage

Salt hydrates are the subject of extensive research for TES applications. The high theoretical energy density of these materials, desorption temperatures achievable with solar thermal collectors and waste heat sources, and discharge temperatures appropriate for room heating and other low-temperature heating applications are the main reasons for this concentration and for the production of hot water for the home^[26]. Owing to the technical limitations of salt hydrates, research at the material level is now underway and will be discussed in more detail. Numerous salt hydrates have been studied for TCES applications; the most commonly used materials are lithium chloride (LiCl), lithium bromide (LiBr), potassium carbonate (K_2CO_3), sodium phosphate (Na_3PO_4), magnesium sulfate ($MgSO_4$), magnesium chloride ($MgCl_2$), sodium sulfite (Na_2S), calcium chloride ($CaCl_2$), and lithium chloride (LiCl)^[9,24,27–29]. Several salt hydrates have been studied and assessed in several scientific publications.

Clark et al. conducted an experimental screening of salt

hydrates for TCES applications in building heating^[28]. The selection criteria included a volumetric energy density >500 kWh/m³, a maximum dehydration temperature of 100°C, and a material cost of less than \$3.5/kg. The substance must also not be dehydrated, flammable, explosive, corrosive, or hazardous. These parameters served as the basis for the selection of $MgSO_4$, $SrBr_2$, $SrCl_2$, Na_3PO_4 , and $MgCl_2$ as the salts. Nonetheless, $SrBr_2$ and $SrCl_2$ are the most promising salts. Additionally, Yan et al. investigated the relationship between phase change and dehydration in salt hydrates ($Na_2SO_4 \cdot 10H_2O$, $CH_3COONa \cdot 3H_2O$, $MgSO_4 \cdot 7H_2O$, and $SrBr_2 \cdot 6H_2O$)^[30]. Rapid heating produces molten hydrates, which dehydrate more slowly and require greater activation energy. Using melting enthalpy and entropy, the equilibrium curve for the direct molten-hydrate dehydration of $SrBr_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ was determined, as illustrated in Figs. 3a and 3b^[30]. Similarly, for $SrCl_2 \cdot 6H_2O$, the thermodynamic equilibria of its various phases were determined. Notably, excellent agreement is observed among the available experimental data concerning the metastable branches. A complete humidity-temperature phase diagram for the $SrCl_2 \cdot H_2O$ system is presented in Figs. 3c and 3d^[31].

Soukpo et al. performed a multistep screening of 125 salt hydrates. They evaluated the material cost, toxicity, dehydration temperature, and storage density, among other factors. Forty-five preselected salts were subjected to hydration/dehydration testing, thermogravimetric analysis, and theoretical calculations. Modified thermogravimetric analysis and differential scanning calorimetry were used to mimic the dehydration (charging) and hydration (discharging) processes. A storage system with a minimum outlet (discharging) temperature of 60°C would meet residential hot water and heating needs, as intended. Finally, $SrBr_2$, $MgSO_4$, and lanthanum chloride ($LaCl_3$) are the most promising TCES materials^[32]. Additionally, Richter et al. evaluated 308 salt hydrates for waste heat recovery at temperatures up to 300°C. $SrBr_2$ matched all the requirements after its reversibility and cycling stability were theoretically and experimentally determined. It achieved a volumetric storage density of 140 kWh/m³ (0.504 GJ/m³) in an open system, and the $SrBr_2$ hydration reaction remained stable for 10 cycles^[33]. $MgCl_2$ is a popular option for low-temperature applications ($<100^\circ\text{C}$), whereas $Ca(OH)_2$ is suitable for intermediate temperatures (400–650°C)^[17,34].

Essen et al. evaluated $MgSO_4$, $Al_2(SO_4)_3$, $CaCl_2$, and $MgCl_2$ and reported that $MgCl_2$ is the most promising, with a potential energy density of 2.8 GJ/m³ (~ 777.78 kWh/m³). However, after hydration, $MgCl_2$ and $CaCl_2$ produced gel-like materials that prevented substantial water uptake^[35]. Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) has also been extensively investigated^[36–41]. Although it has a high theoretical energy storage capacity of 2.27 MJ/m³ (~ 0.63 kWh/m³) (from heptahydrate to monohydrate), its efficiency is limited during repeated cycles because of slow reaction kinetics and partial irreversibility in practical applications. The formation of the amorphous phase during the dehydration of $MgSO_4 \cdot 6H_2O$, which is associated with a slow, inhomogeneous reorganization of the crystal structure, can lead to a very slow temperature rise when air is used as the HTF. However, the lower heat release of $MgSO_4 \cdot 7H_2O$

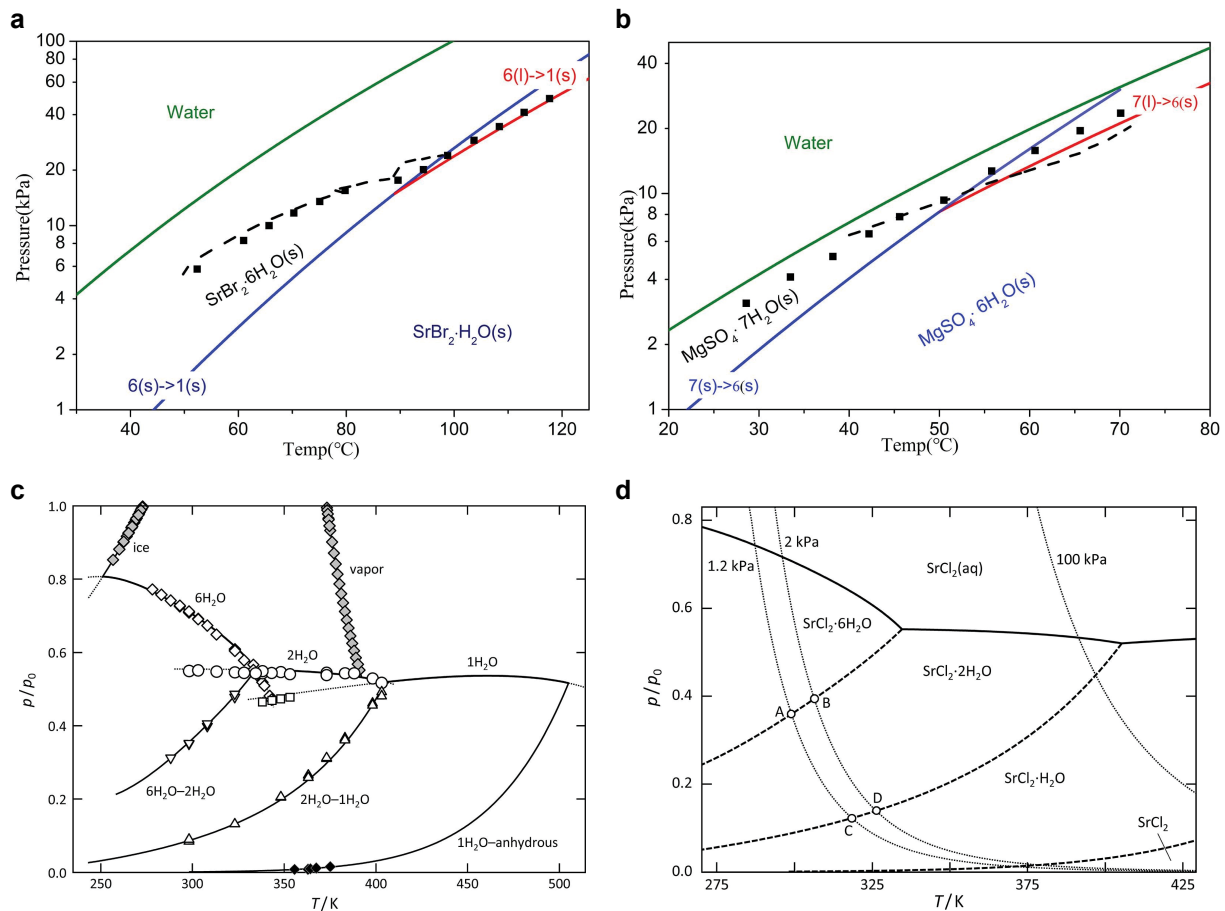


Figure 3 Phase diagrams illustrating the thermal and hygroscopic behavior of hydrated salt systems for TCES: (a) Depicts the melting and dehydration pathways of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$. The black dashed line traces the dynamic phase-change route, showing that the solid hexahydrate can either melt $[6(\text{l})]$ or dehydrate directly into the solid monohydrate $[6(\text{s}) \rightarrow 1(\text{s})]$, with the equilibrium point marked by a black rectangle. (b) Presents the corresponding behavior of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, where the dashed line indicates that heating primarily triggers step-wise dehydration from the solid heptahydrate to the hexahydrate $[7(\text{s}) \rightarrow 6(\text{s})]$ rather than melting, although the molten state $[7(\text{l})]$ remains possible under certain conditions. Reproduced with permission from Ref. [30] ©2019, Elsevier Ltd. (c) Provides a comprehensive humidity-temperature phase diagram for the $\text{SrCl}_2\text{-H}_2\text{O}$ system, mapping stability zones for each hydrate phase; inverted triangles mark the hexahydrate-dihydrate equilibrium, triangles represent the dihydrate-monohydrate transition, and black diamonds indicate the monohydrate-anhydrous equilibrium, while white diamonds, circles, and squares denote deliquescence points where each salt form dissolves in absorbed moisture; solid lines represent calculated phase boundaries, and dotted lines indicate metastable conditions. (d) These relationships are simplified by using solid lines to show deliquescence boundaries (where salts absorb moisture and dissolve), dashed lines to represent hydration equilibrium (where water molecules are taken up or released), and dotted lines to indicate constant water vapor pressure isobars at 1.2 kPa, 2 kPa, and 100 kPa, respectively, providing practical operating parameters for system design. Reproduced with permission from Ref. [31] ©2018, Elsevier Ltd.

is due mainly to the amorphization of the material during dehydration at 13 mbar, which reduces its sorption capacity upon rehydration. According to the literature, the conversion of hexahydrate to monohydrate is the most promising reaction^[38,39].

Donkers et al. evaluated 25 hydrated salts for building heating, targeting a storage density $>1.3 \text{ GJ/m}^3$ ($\sim 361 \text{ kWh/m}^3$), a discharge temperature $>50^\circ\text{C}$, and a desorption temperature $<120^\circ\text{C}$. Na_2S , GdCl_3 , and EuCl_3 offered the highest energy densities, whereas MgCl_2 was the most cost-effective option^[23]. For medium-temperature applications ($150\text{--}300^\circ\text{C}$), the most promising method is SrBr_2 . Figures 4a and 4b illustrate that it maintained a high-power performance of up to 4 kW/kg during hydration over 100 cycles, with an energy density of 291 kJ/kg (178 kWh/m^3). Although the dehydration rates

decreased after 100 cycles, the process remained reversible. However, the high material cost of pure SrBr_2 remains the main barrier to large-scale deployment^[42].

Kiyabu et al. Computational screening of hydration reactions for new TES materials and design rules based on energy density, cost, and temperature hysteresis. Seventeen interesting hydration reactions were selected from 265 hydration reactions that underwent computational screening. The three reactions for each of the six different temperature groups are shown in Fig. 4c. Reactions that failed to satisfy the hysteresis limitation were eliminated. Notably, because they surpassed the 50°C hysteresis limit, all reactions below that temperature were eliminated. Additionally, only two potential reactions were found in the $450\text{--}600^\circ\text{C}$ range; the remaining candidates were eliminated since they involved costly platinum. Among these

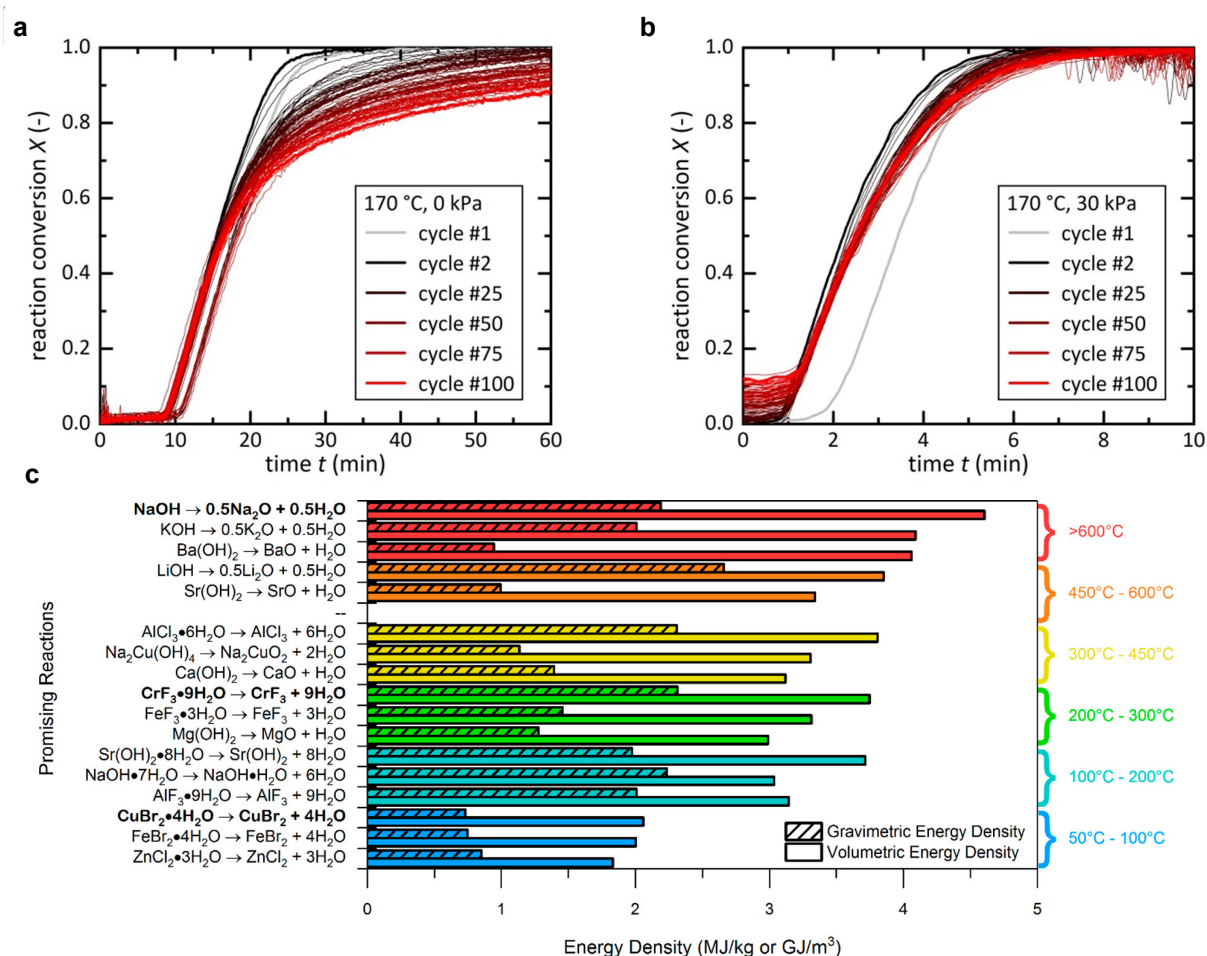


Figure 4 Performance and classification of TCMs: (a–b) Isothermal cycling stability of SrBr₂ showing dehydration at 170°C in dry nitrogen and hydration at 170°C under 30 kPa water vapor pressure over multiple cycles. Reproduced with permission from Ref. [42] ©2020, Elsevier Ltd. (c) Temperature-based sorting of promising TES reactions with gravimetric and volumetric energy densities, highlighting top performers for low (<100°C), medium (100–300°C), and high (>300°C) temperature applications. Reproduced under the CC BY 4.0 license from Ref. [43] ©2018, American Chemical Society.

17 reactions, more than one-third appear to be absent from the TES literature. These potentially new reactions involve the following six compounds: AlF₃·9H₂O, CrF₃·9H₂O, FeBr₂·4H₂O, Na₂Cu(OH)₄, NaOH·7H₂O, and ZnCl₂·3H₂O. As part of this screening process, two property-performance databases were also created: one for hydrates and one for hydroxides^[43].

The most salt-hydrated TCHS, which includes SrCl₂, SrBr₂, MgSO₄, MgCl₂, K₂CO₃, and Na₂S, is assessed for sorption suitability on the basis of four factors: cost (low-cost availability), ESD (e.g., theoretical up to 778 kWh/m³ for MgSO₄), safety (nontoxicity preferred), and operating temperature (usually <200°C to match low-grade heat). SrBr₂ offers balanced performance in open systems; CaCl₂ and MgCl₂ offer high densities but are prone to deliquescence, and MgSO₄ stands out as extremely promising because of its higher energy density, despite its slow kinetics. K₂CO₃ has the potential to improve the kinetics of composites, which often require embedding in a matrix, such as silica gel or vermiculite, to promote mass transfer and reduce issues such as leakage. The toxicity and corrosivity of Na₂S restrict its application^[8,24,28,29]. The use of

salt hydrates in TCHS is complicated by the way these devices operate. These challenges include agglomeration, deliquescence, chemical instability, and mechanical instability^[25,44,45]. Dehydration is the process by which salt hydrates store energy, and hydration is the process by which they incorporate water molecules into their crystal structure. Because water molecules are added and removed during hydration and dehydration, structural modifications and volume changes accompany these processes. These structural changes generate mechanical stresses in the material as the number of hydration/dehydration cycles increases, leading to mechanical instabilities, including formation, fracture, and cracking^[25,45,46].

Second, at high water vapor pressure, another phase shift occurs because salt hydrates are hygroscopic. This phase shift, deliquescence, is often referred to as “overhydration” in the literature. During deliquescence, the salt hydrate absorbs more water than its crystal lattice can hold, producing a saturated solution. This transition is associated with higher energy densities than hydration^[47–49]. The material is no longer suitable for heat storage because of salt agglomeration resulting from repeated drying of the

deliquescent salt. The swelling and clumping of salt hydrates in a crowded bed is the third issue^[25,44]. The thermophysical properties and performance characteristics of representative hydrated salts used in TCHS are summarized in Table 1.

However, owing to their low cyclability, agglomeration, and thermal conductivity, these materials require improvement. The idea of increasing heat conductivity by adding conductive carbon-based materials, such as carbon nanotubes (CNTs), has shown promise. Therefore, the effects of recently published methods on heat and mass transfer appropriate salt hydrates are matched to various materials, composites, and structural optimization mixing pairs^[60,61].

4 Composite materials for thermochemical heat storage

As previously mentioned, the widespread use of salt hydrants in TCES systems is associated with several material-related problems. Pure salt has low porosity and poor heat and mass-transfer properties, making its use impractical. Effective energy storage through gas-solid reactions requires a sufficient reaction surface area between the salt and water vapor. Additional material problems that limit the practical use of pure salts include agglomeration and caking, deliquescence, and limited thermal conductivity. Several material enhancement techniques, such as the use of mixed salts and the incorporation of a porous matrix, have been developed to address these problems. The term “composite” is most commonly used to describe these systems. A salt in a porous matrix composite is a hybrid material in which a salt hydrate is embedded within the pores of a solid support, such as silica gel or expanded graphite. This combination enhances thermal stability and sorption performance for applications in energy storage and humidity control^[62,63].

In accordance with Levitskij et al., a composite was made of silica gel and CaCl_2 ^[64]. The properties of these

composites lie between those of inorganic salts and those of the porous support^[65]. A salt in a porous matrix composite is a dual-function material that combines the heat of adsorption of the porous matrix with the heat of hydration of the salt hydrate to enhance energy performance^[66]. In salt-in-porous matrix composites, two distinct sorption mechanisms operate simultaneously. Physical adsorption occurs when van der Waals forces cause H_2O to adsorb onto the sorbent surface, within zeolite pores, and within the internal pores of the matrix. Concurrently, in salt hydration reactions, chemical sorption, sometimes referred to as chemisorption, involves the formation of molecular bonds between water vapor and salt hydrates, enabling higher ESD through reversible chemical reactions. Numerous porous matrices have been investigated to date. These include MOFs^[67,68], CNTs^[69], expanded graphite (EG)^[70], vermiculite^[71–73], metal foams^[74,75], silica gels^[76–79], activated carbons^[80,81], porous supports, synthetic and natural zeolites^[82–86] and various natural clays^[87–91]. Table 2 provides a comparative overview of the distinct characteristics, advantages, and limitations of these composite material families for TCHS. They are commonly used. Extensive experimental evidence and theoretical studies indicate that composite adsorbents offer several key advantages^[65,105].

An ideal support matrix must have high porosity and a large surface area to ensure efficient vapor transport, complete hydration reactions, and high salt loading capacity. The matrix needs to be highly thermally conductive to enable effective heat transfer within the composite. To withstand numerous cycles without structural disintegration, mechanical integrity is essential. Chemical compatibility with salt is essential for preventing unwanted reactions, degradation, or gradual loss of function. Additionally, the matrix needs to be highly hydrophilic to enable effective interaction with water vapor and sufficiently inert to prevent deliquescence or early hydration under ambient conditions. Ideally, it should be inexpensive, widely available, and environmentally friendly to enable

Table 1 Performance comparison of typical hydrated salts in TCHS systems.

Hydrated salt	Dehydration/hydration (°C)	Theoretical volume energy density (kWh/m ³)	Key advantages and uses	Key disadvantages and challenges	Refs.
Strontium bromide	90–120 28–48	627.8–691.7	High energy density, good thermal stability	Prone to overhydration, low-to-medium temperature heat storage	[9,50]
Strontium chloride	42–50 27–28	561.1–697.1	High energy density, excellent stability	High cost	[9,51]
Magnesium sulfate	100–150 ~88	528–806	Long-term heat storage and seasonal storage are low-cost and readily available, and raw material costs are low	Incomplete reversible reactions are prone to occur	[41,52]
Potassium carbonate	65–120 ~59	344–361	Chemically stable and nontoxic, low cost	Relatively low energy density	[8,53]
Calcium chloride	30–200 ~43	694.4–805.5	Heating, ventilation, and air conditioning systems, dehumidification, low cost, and abundant resources	Poor stability in pure salt circulation, severe deliquescence	[54–56]
Magnesium chloride	96–117 ~61	305.6–536.1	Low raw material costs and abundant resources	Severe deliquescence, poor circulation stability	[8,57]
Sodium sulfide	82–100 ~66	738.9–775.0	Extremely high energy density	Highly toxic, highly corrosive	[8]
Sodium hydroxide	50–100 ~40	1388.9	Industrial heat storage, chemical industry, low cost	Highly corrosive	[58]
Copper sulfate	50–150 ~78	638.9	Good energy density, heat recovery systems	Corrosive, slow reaction kinetics	[59]

Table 2 Comparison of distinct characteristics of composite families for TCHS.

Composite family	Host structure	Salt example	Distinct advantage	Distinct limitation	Best suited for	Refs.
Carbon-based	Porous carbon, graphene	LiBr CaCl ₂	Highest thermal conductivity enhancement, rapid heat dissipation	Low salt loading capacity complex synthesis	Fast cycling, high-power applications	[80,92–94]
Silica-based (SiO ₂)	Mesoporous silica	MgSO ₄ CaCl ₂	Excellent salt confinement prevents deliquescence, and good cyclic stability	Moderate thermal conductivity, expensive template synthesis	Long-term stability, deliquescence-prone salts	[78,90,95,96]
Zeolite-based	Microporous aluminosilicate	CaCl ₂ Na ₂ SO ₄	High surface area, operates over a wide T/humidity range, low-temperature suitability	Microporosity limits mass transfer and slows kinetics	Low-temperature applications (e.g., building heating)	[80,97,98,99]
MOF-derived	MOF (MIL-53 ZIF-8)	Salt@MOF NPC-Al	Ultrahigh porosity (> 2000 m ² /g) tunable pore architecture	High synthesis cost; limited scalability	High-density storage, lab-scale demonstrations	[100,101,102]
Mineral-based	Vermiculite, perlite	MgSO ₄ CaCl ₂	Very low-cost, high pore volume, strong water retention	Small surface area swelling/shrinking, poor cycle-to-cycle mechanical stability	Low-cost, large-scale, stationary storage	[9,103,104]

widespread use^[106].

4.1 Zeolite-based composites for thermochemical heat storage

Owing to their strong structural stability and high water adsorption capacity, microporous aluminosilicate minerals called zeolites are frequently used as effective supporting matrices in open TCES systems. High ESD is enabled by the intrinsic nanopore structure, which provides robust encapsulation of hygroscopic salts and physical sorption sites. To maximize pore filling and mass transfer, the pore structure of the zeolite must be well matched to that of the chosen salt. According to previous studies, performance depends on optimizing salt loading to balance structural strength and storage capacity^[107,108].

The MgSO₄@13X zeolite composites (denoted as 13X/X, where X represents the MgSO₄ solution concentration, wt.%) were prepared by solution impregnation for long-term TCHS. Increasing MgSO₄ loading enhanced water uptake and heat storage density despite reduced BET surface area and pore volume due to salt deposition. The composites showed excellent chemical compatibility, and heat storage density increased with increasing RH and MgSO₄ content (Fig. 5a). For example, A-13X/15 increased its heat storage density from 530 to 632 J g⁻¹ as RH increased from 50% to 80%. These results demonstrate that MgSO₄ incorporation improves heat storage performance through enhanced hydration capacity and water affinity^[97]. The data in Fig. 5b imply that ZnSO₄·7H₂O was modified via impregnation with zeolite matrices (13X-zeolite) and Linde Type A (LTA-zeolite) to improve its hydration performance. The water sorption capacity of the composites was tested in a controlled-temperature, controlled-humidity environment. The ZnSO₄/13X-zeolite composite exhibited the highest water sorption (0.26 g/g) at 75% RH and 45°C, which is double that of pure ZnSO₄·7H₂O. This improvement is attributed to the large surface area (491 m²/g) and pore volume (0.31 cm³/g) of the composite. The hydration rate and adsorption mass were found to depend on both the RH and temperature; however, the performance significantly decreased when the conditions exceeded 45°C and 75% RH. Furthermore, XRD analysis of the ZnSO₄/13X composite confirmed that the crystallinity and phase of the partially hydrated ZnSO₄

remained stable throughout the sorption–desorption process, enhancing the adsorption mass and enthalpy during hydration^[109]. According to Xu et al., the MgCl₂@zeolite composite achieved a maximum water uptake of 0.55 g g⁻¹, with gravimetric and volumetric energy densities of 1368 kJ kg⁻¹ and 308 kWh m⁻³, respectively, at a charging temperature of 200 °C (Fig. 5c). The enhanced performance is attributed to the synergistic combination of physisorption, chemisorption, and liquid-phase absorption, while the sorption behavior of 13X, NaMgX, and MgCl₂@ZEO_22 demonstrates the strong influence of operating conditions on thermal storage performance^[110].

The sorption capacity increases with increasing RH and with increasing hydration temperature, typically below 50°C. This presents a significant disadvantage: the adsorption potential of MgSO₄@zeolite sorbents decreases markedly when the hydration temperature exceeds 50°C, whereas ZnSO₄@zeolite-13X composites lose their hydration capacity at 45°C^[111,112]. System-level evaluations indicate potential despite these thermal constraints. Although they might not fully meet a household's heating needs, conceptual designs that combine zeolite/salt composites with flat-plate solar thermal collectors are economically viable for residential interseasonal energy storage^[113]. Additionally, to improve mass transfer and stabilize the structure 3AM, 5AM, and 13XM composites were prepared using 10% and 20% MgSO₄ solutions. Although 3A- and 5A-based composites exhibited higher MgSO₄ loadings, their smaller pore sizes promoted surface salt deposition and pore blockage. In contrast, the mesoporous structure of 13X zeolite enabled uniform MgSO₄ dispersion with minimal pore plugging, resulting in superior mass transfer. Consequently, the 13XM20 composite achieved the highest water sorption capacity (0.21 g g⁻¹ at 25 °C and 60% RH; Fig. 5d) and exhibited favorable structural characteristics (Figs. 5e–i). Accordingly, the 13X/MgSO₄ composite delivered the best heat storage performance, with a heat storage density of 87.7 kWh m⁻³, highlighting its potential for low-grade industrial waste heat and solar thermal energy storage^[114].

Zeolites, especially type 13X, are microporous, crystalline aluminosilicates with a consistent pore structure, strong thermal stability, and high water affinity. They can

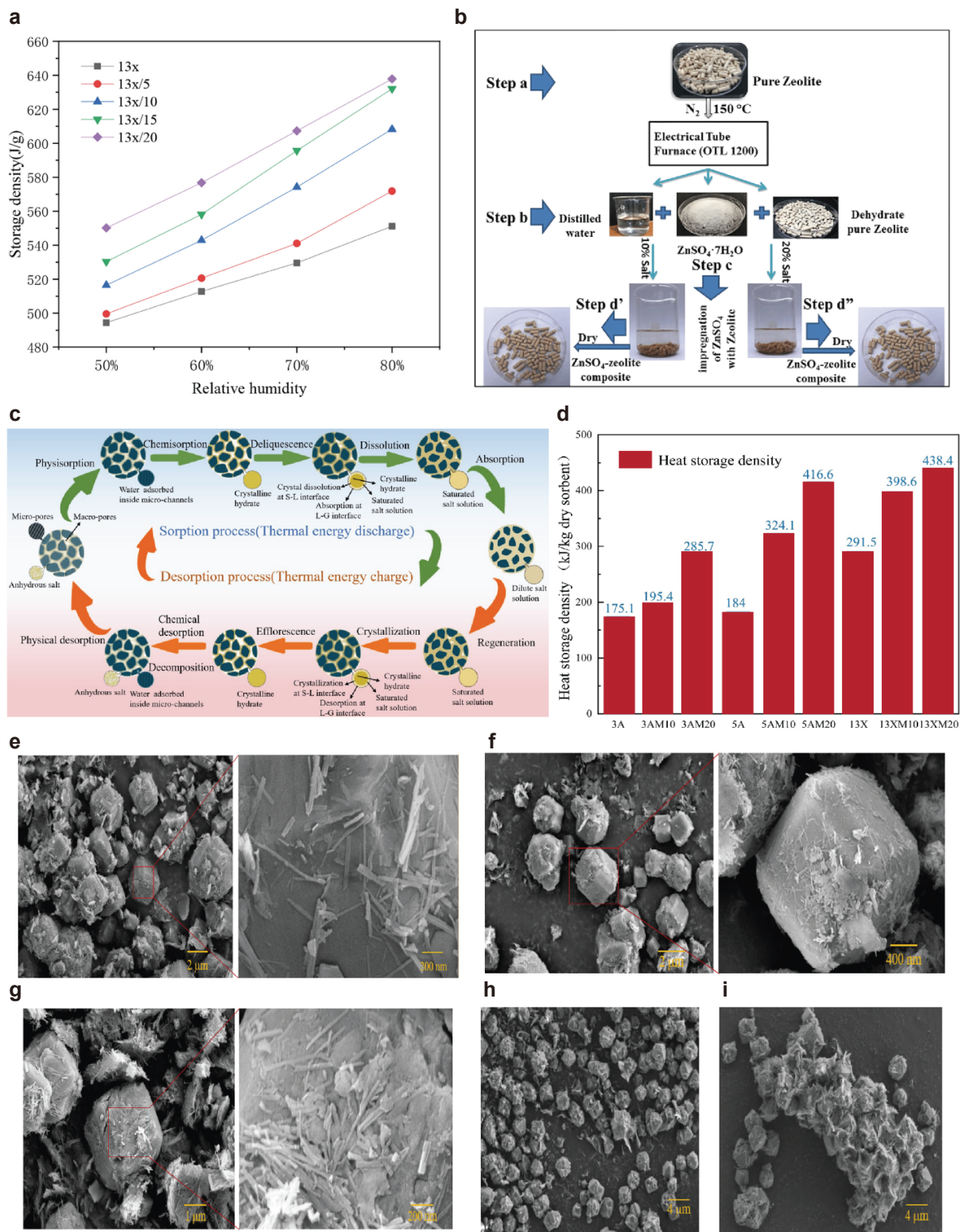


Figure 5 Performance and stability of composite TCMs: (a) The heat storage densities of 13x/X and 13X at different RH levels. Reproduced with permission from Ref. [97] ©2019, Elsevier B.V. (b) The preparation procedures of the ZnSO_4 -zeolite composite. Reproduced with permission from Ref. [109] ©2019, John Wiley & Sons, Ltd. (c) The working principle of multistep thermochemical energy storage is based on multistep sorption–desorption processes. Reproduced with permission from Ref. [110] ©2019, Elsevier Ltd. (d) The heat storage density of 3A, 5A, and 13X zeolites and their corresponding composite sorbents. (e–i) SEM images of 3AM10, 5AM20, 5AM10, 13XM10, and 13XM20 composite sorbents respectively. Reproduced with permission from Ref. [114] ©2024, Elsevier Ltd.

achieve high energy densities of 55.7–166.7 kWh/m^3 (0.2–0.6 GJ/m^3) in cycles with load temperatures exceed-

ing 150°C, and their pore widths typically range from 4 to 10 Å^[85,115]. However, zeolite 13X has several notable draw-

backs. Its small pore size and low thermal conductivity (~ 0.15 W/m-K) can cause problems at high salt concentrations, including pore obstruction and salt migration. Ion exchange is another crucial consideration. The characteristics and performance of zeolite 13X may change when it is exposed to salt solutions such as CaCl_2 , as Na^+ ions in its framework may be replaced by Ca^{2+} ions from the solution^[9,66]. This ion exchange can affect the structural support of the zeolite, potentially impacting the overall stability and efficacy of the composite. Therefore, understanding the chemical interactions between the salt and the zeolite support is crucial for the design and optimization of these systems. When a lower-temperature heat source, such as solar panels, is available, the high regeneration temperature required for zeolites poses a significant drawback. Furthermore, poor mechanical strength can lead to sorbent loss and performance degradation, thereby limiting its useful applications.

4.2 Silica gel-based composites for thermochemical heat storage

A common host matrix for TCHS is silica gel because of its high affinity for water vapor, low cost, and ease of regeneration. Research has shown that the porous structure of hygroscopic salts can be effectively modified, resulting in the production of composites with superior cycling stability and high energy storage capacity. Researchers developed a $\text{CaO}/\text{Ca}(\text{OH})_2$ TCHS system for concentrated solar power plants by fabricating mixed $\text{Ca}(\text{OH})_2/\gamma\text{-Al}_2\text{O}_3$ pellets via dip-coating with dense silica and Al-MCM-41 (mesoporous silica) gels^[116]. Adding a 40 wt% alumina binder, together with a silica coating, significantly increased the pellet hardness from less than 2 N to 31 N. Upon calcination, a hard calcium silicate layer formed and maintained structural integrity over 10 dehydration/hydration cycles at 600°C dehydration and 250–425°C hydration (Figs. 6a and 6b). Comparative tests revealed that cylindrical pellets outperformed spherical pellets in terms of both hardness and hydration yield. After cycling, the porous silica-coated cylindrical pellets achieved an 85% hydration yield while maintaining an 8 N hardness (Fig. 6c). This superior performance was attributed to their porous structure and thin-sheet coating composition, which preserved outer porosity throughout repeated cycling^[116]. Additionally, Yan et al.^[117] fabricated core-shell pellets with $\text{Ca}(\text{OH})_2$ as the core and silicon carbide as the shell. The resulting pellets exhibited good cycling stability, consistent size, and stable shape (Fig. 6d). Researchers have experimentally validated the heat-storage characteristics and mechanical strength of pellets and have simulated their behavior. According to the test results, the heat storage density of the pellets decreased by less than 20% over 25 cycles of heat storage and release, as illustrated in Fig. 6e. Crucially, no crushing or cracking was observed during cycling, demonstrating the structural stability of the core-shell design.

Shervani et al.^[118] created three CaCl_2 -based composites using three distinct stabilization techniques: impregnation into silica gel, encapsulation in methyl cellulose, and a combination of the two. The first composite was prepared by impregnating silica gel with CaCl_2 . The second composite consisted of methyl cellulose-encapsulated CaCl_2 . In the

third composite, a two-step process was used: First, CaCl_2 was impregnated into the silica gel, and then the CaCl_2 was encapsulated in methyl cellulose. Among these three formulations, the CaCl_2 -impregnated silica gel encapsulated in methyl cellulose performed best. This composite exhibited reasonable stability and maintained energy-storage performance after three hydration/dehydration cycles, with minimal agglomeration. Under testing conditions of 90% inlet RH after regeneration at 90°C, this material achieved an energy storage density of 241 kWh/m³ (0.87 GJ/m³) and a specific energy of 630 Wh/kg (2268 kJ/kg). Calabrese et al.^[119] incorporated $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ into a siloxane polymer matrix at weight percentages of 40%–70%, yielding a stable TES composite foam, as shown in Fig. 6f. Scanning electron microscopy (SEM) was performed to better visualize the distribution of salt in the silicone foam. This design effectively mitigates common issues with salt hydrates, such as corrosion and swelling. The evenly distributed, interconnected pore network of the foams enables efficient water vapor transport, as evidenced by high-magnification scanning electron microscopy. After 50 compression cycles, the material retained 87% of its salt hydrate content, demonstrating exceptional mechanical stability and suggesting strong durability for real-world applications (Figs. 6g and 6h).

Courbon et al.^[78] developed a high-performance silica gel/ CaCl_2 composite using a repeated impregnation-drying method, achieving a maximum salt loading of 43 wt%. The composite's success depends on an optimized pore structure, in which small pores are filled with salt while larger pores remain partially open to promote vapor diffusion. The addition of CaCl_2 significantly increased both the amount of water sorbed and the heat released during operation. Among the materials tested, the silica gel/ CaCl_2 composite exhibited the highest sorption capacity (0.27 g/g) and a heat storage capacity of 166 kWh/m³. Under practical operating conditions, it achieved a superior volumetric heat storage density of 211 kWh/m³ (~ 760 kJ/kg) and excellent stability over 10 cycles, with no salt leakage. The activation energy for the desorption process followed the order of silica gel/ CaCl_2 < bentonite/ CaCl_2 < alumina/ CaCl_2 . Thermogravimetric analysis curves and differential thermogravimetry (DTG) curves of the three CaCl_2 -based composites are shown in Figs. 6i and 6j. This trend was the opposite of the pore sizes of the various composites, with silica gel-based materials having the largest pores^[89]. For TCES, silica gel is a popular and reasonably priced host matrix that provides an appropriate charging temperature^[62]. Preventing salt deliquescence and leakage under high salt concentrations or RH, which impair performance and stability, is a major challenge^[79,120].

4.3 Carbon-based composites for thermochemical heat storage

Carbon-based materials, including expanded natural graphite (ENG), multiwalled carbon nanotubes, and activated carbon (AC), serve as effective matrices for composite TCHSs. Their large pore structure and exceptionally high thermal conductivity are crucial for rapid charging and discharging. Mesoporous material ENG has numerous applications. When ENG is treated with salts such as

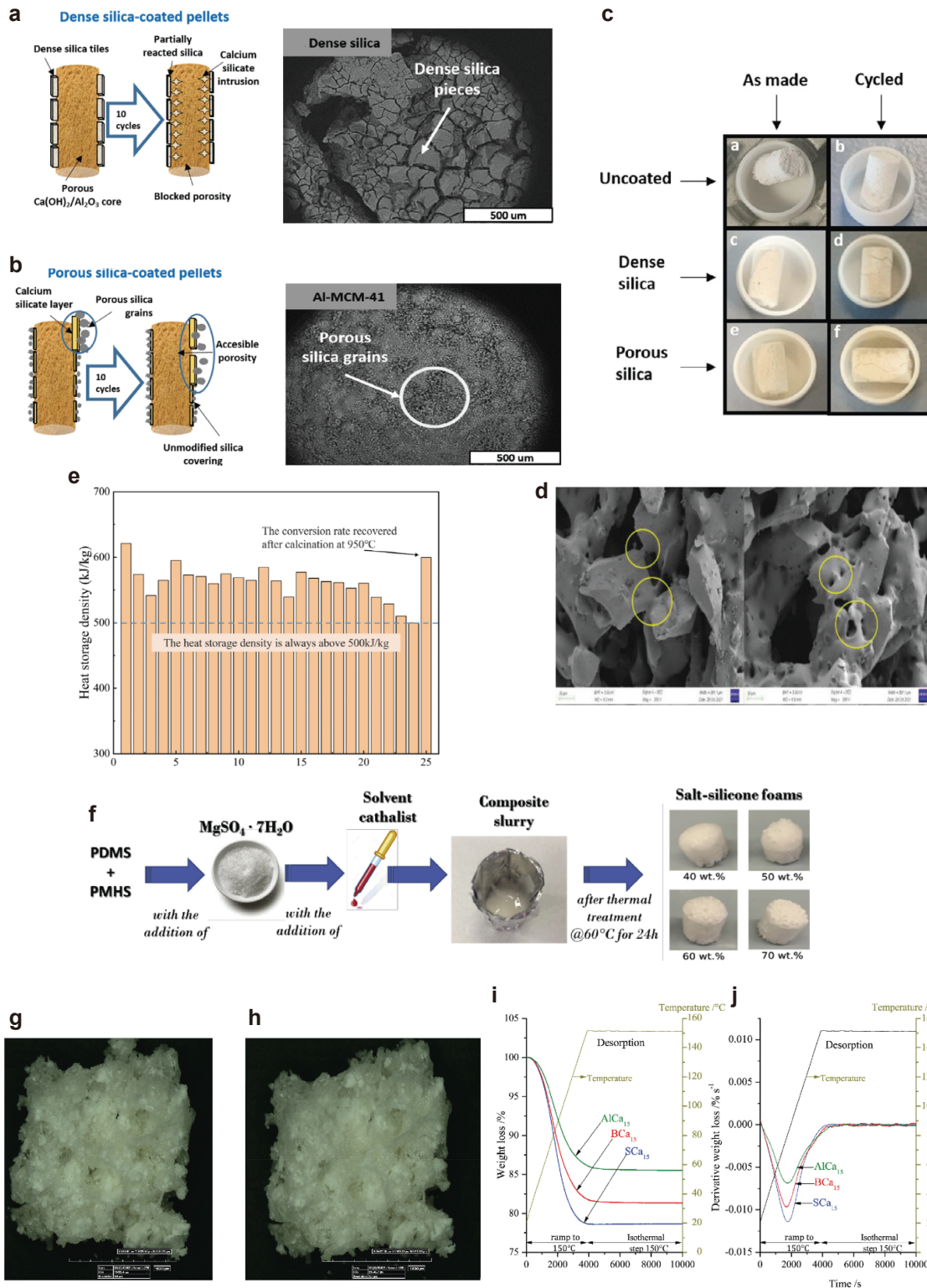


Figure 6 Performance enhancement strategies for TCHS materials: (a–b) Hydration capacities over 10 cycles and hardness values before and after cycling for $\text{Ca(OH)}_2/\gamma\text{-Al}_2\text{O}_3$ cylindrical pellets with a silica coating. (c) Cylindrical pellets before and after 10 dehydration/hydration cycles at $600^\circ\text{C}/425^\circ\text{C}$. Reproduced under the CC-BY-NC-ND license from Ref. [116] ©2022, The Authors. (d) Connections formed between silicon carbide particles. (e) Core-shell-structured SiC@Ca(OH)_2 composite showing heat storage density variation with charge-discharge cycles. Reproduced with permission from Ref. [117] ©2024, Elsevier B.V. (f) Scheme of the preparation steps of salt-silicone foams. (g) and (h) Durability of salt-silicone composite foams, including optical images of F_Mg60 foam before and after 50 cycles of compression testing, demonstrating mechanical stability. Reproduced with permission from Ref. [119] ©2019, Elsevier B.V. (i) and (j) Thermogravimetry (TG) and DTG curves of three CaCl_2 -based composites. Reproduced with permission from Ref. [89] ©2017, Elsevier B.V.

MgSO₄, its specific surface area is significantly reduced. ENGs form a porous host, increase the mechanical strength and compressive resistance of the composite, improve its corrosion resistance, and establish a high-conductivity network^[70]. ENGs effectively mitigate the mass-transfer limitations common in salt hydrates. For example, when pure SrBr₂ is dehydrated, a dense salt shell forms on the surface, blocking the flow of water vapor and hindering further reactions. However, when SrBr₂ is paired with an ENG matrix, the kinetic lag is significantly reduced because the ENG provides continuous vapor-transfer pathways that bypass the salt shell^[50,121]. To further improve the salt compatibility with graphite, organic poly-electrolytes may be added during composite preparation. In a similar vein, ENG/CaCl₂ composites have been shown to prevent salt clumping and to increase the temperature of hot air in a storage system by approximately 22°C, demonstrating improved heat transfer performance^[49].

The exceptional performance of the LiOH·H₂O/EG composite as a TCM is confirmed by a thorough analysis. Because EG serves as a porous matrix, salt hydrates can be distributed evenly across its macropores and interlayers. At 30°C and 60% RH, the EG8 composite, containing 8% EG, exhibits a high practical ESD of 1120 kJ/kg (~249 kWh/m³); even higher capacities are achievable at higher humidity levels. A crucial improvement is the thermal conductivity of the composite (6.52 W/(m·K)), which is 6.5 times greater than that of pure LiOH·H₂O. The relationships among the EG concentration, ESD, and thermal conductivity are shown in Fig. 7a. Moreover, the EG8 composite exhibits remarkable cycle stability, which is a critical advantage for practical applications. After 10 hydration/dehydration cycles, the ESD of pure LiOH·H₂O decreases by 31.4%, whereas that of the EG8 composite is maintained at 280.6 kWh/m³ (1010 kJ/kg), representing a reduction of only 9.8%. This enhanced stability is accompanied by improved sorption kinetics, with EG doping lowering the activation energy from 62.7 kJ/mol (for pure salt) to 59.5 kJ/mol, thereby reducing the dehydration temperature. System-level simulations further confirm the engineering potential of the material for practical applications. A thermal storage unit using the EG8 composite achieves 83.6% charging thermal efficiency, demonstrating its viability for real-world implementation in home heat storage systems^[122].

To improve the control and stability of salt organization within the composite structure, researchers have developed strontium bromide-graphite-nanocellulose composites, as illustrated in Fig. 7b. This approach enhances mass and heat transport during salt hydration and dehydration cycles while optimizing the air/salt and salt/graphite interfaces. Composite characteristics are strongly influenced by the fabrication process. Freeze-drying produces highly porous structures with directed channels that facilitate moisture transport throughout the composite, whereas wet impregnation yields materials with limited porosity. With an ESD of up to 764 kJ/kg (~85 kWh/m³) (48% higher than the theoretical value), the organic binder actively contributes to energy storage as compared with pure salt, freeze-dried nanocellulose composites show a notable 54% improvement in hydration kinetics^[123].

In a related breakthrough, scientists reported that incorporating 1% CNTs into MgSO₄/zeolite composites increases the thermal conductivity by 35%, indicating another successful method for improving composite performance^[124]. Core-shell CaCl₂@C composites were synthesized via a one-pot pyrolysis process from coal tar as the carbon precursor. In this structure, CaCl₂ was successfully loaded into the mesopores and macropores of the hierarchical porous carbon shell. This approach enhances structural stability, prevents salt agglomeration and solution leakage, and offers several advantages over simple impregnation techniques. Under simulated sunlight at 1000 W/m², the carbon shell enabled efficient light-to-heat conversion, reaching a surface temperature of 75°C (Fig. 7c). After 230 minutes of continuous irradiation, the composite achieved a high volumetric ESD of 254 kWh/m³, with a water uptake of 0.81 g H₂O per gram sorbent. These results demonstrate the material's strong potential for integrated solar thermal conversion and storage applications^[125]. Additionally, Wei et al.^[126] developed a core-shell composite with a high CaCl₂ concentration of 56.5%. The material features an expanded perlite (EP) core with CaCl₂ filling its macroporous structure. A thin photothermal carbon shell, comprising 5.9% of the material, envelops the core, absorbing sunlight and generating heat that desorbs the salt hydrates within. The resulting sorbent, EP/Ca@C-0.25, has a high adsorption capacity of 1.22 g-H₂O per gram of sorbent at 20°C and 80% RH. The data in Figs. 8a–8d indicate that the thin carbon shell efficiently drives desorption under simulated sunlight at 1 kW/m², achieving 84% conversion in 2 h and a sorbent heat storage density of 1698 J/g (~283 kWh/m³) per cycle. The dual confinement provided by the EP matrix and the carbon shell promotes structural stability. During the subsequent heat-release phase, the material maintained a raised outlet air temperature of 36.5°C, demonstrating its potential for practical applications such as room heating. The high cyclic durability of the composite for long-term solar thermal energy storage was confirmed by favorable, humidity-dependent sorption kinetics and a stable capacity of 0.69 g-H₂O per gram of sorbent over 15 cycles^[126].

The data in Figs. 7d and 7e imply that the AC was investigated as a porous matrix for the AC-CaCl₂ TCHS composites, revealing that larger pore volumes directly increase the CaCl₂ content, water absorption, and heat storage density. The mesopore-dominant AC₃/Ca composite achieved a superior heat storage density of 2981 kJ/kg (~497 kWh/m³) with a water uptake of 1.07 g/g and retained 89.76% of this capacity after 25 cycles. A kinetic analysis further revealed that the water absorption mechanism is governed by intraparticle diffusion within the AC pores. SEM and EDS images of AC₃/Ca after 25 cycles (Figs. 7f–7i)^[80]. Similarly, composites were successfully prepared by incorporating AC with Na₃PO₄ via melt impregnation (Fig. 7j). The addition of AC shortened the time required for the composites to reach hydration equilibrium, with higher RH leading to greater water absorption across all the samples. The volumetric heat storage density increased with both the humidity and Na₃PO₄ mass fraction; for example, the R-AC@Na₃PO₄-80% composite achieved a density of 2153 J/cm³ at 80% RH. However, the increase in storage density diminished at

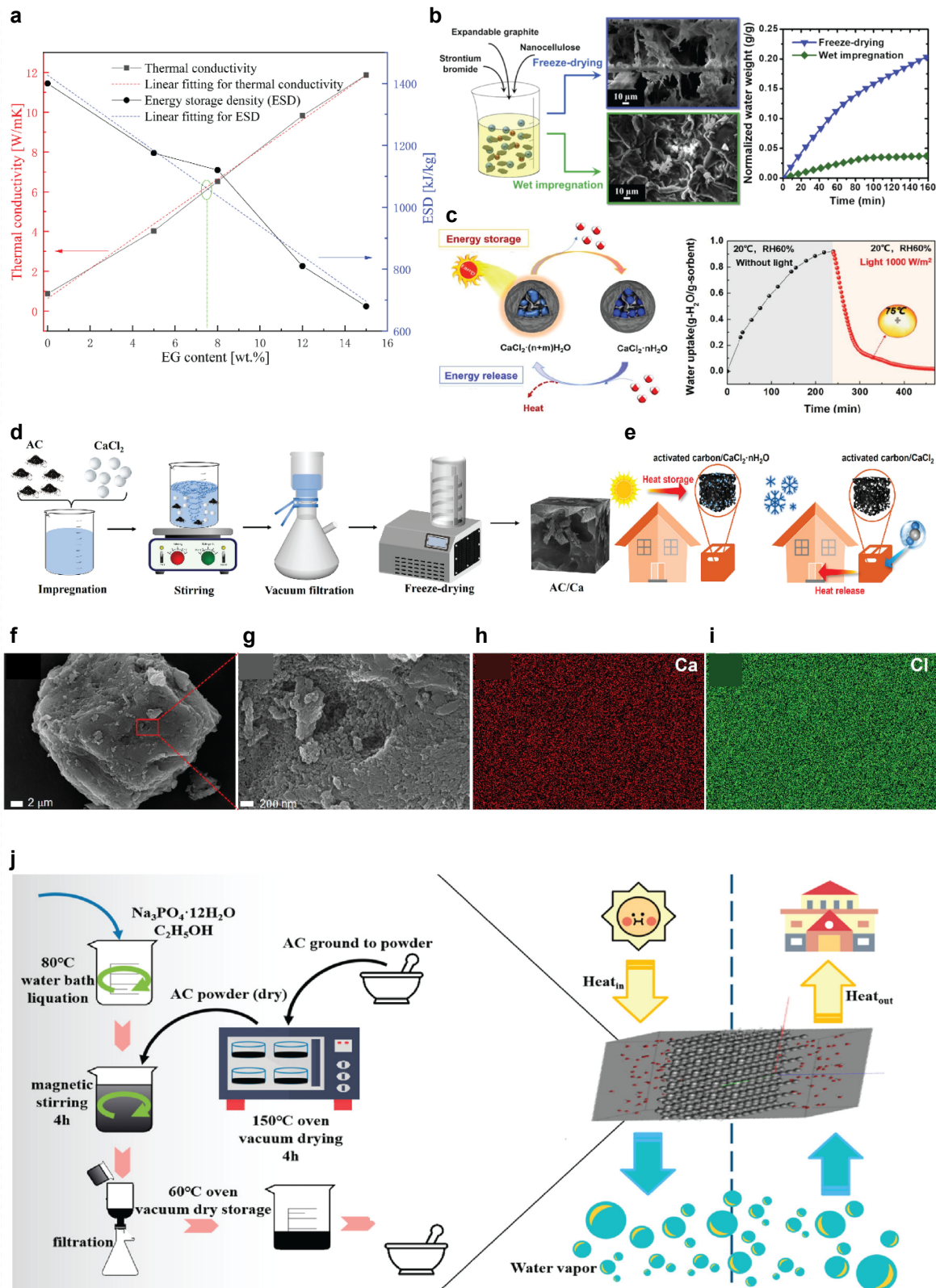


Figure 7 Advanced composite preparation and performance for TCES: (a) Effect of the EG mass content on the heat storage density and thermal conductivity of the composite TCMS. Reproduced with permission from Ref. [122] ©2020, Elsevier Ltd. (b) Freeze-drying fabrication of nanocellulose-based foam. Reproduced with permission from Ref. [123] ©2020, Elsevier Ltd. (c) Core-shell CaCl_2 @C composites enable more stable and efficient TCES processes. Reproduced with permission from Ref. [125] ©2020, Elsevier Ltd. (d-e) Schematic diagram of carbon/ CaCl_2 composites and their application process. (f-i) SEM and EDS images of AC_3/Ca after 25 cycles. Reproduced with permission from Ref. [80] ©2024, Elsevier Ltd. (j) Flow chart of the preparation of activated carbon-based Na_3PO_4 composites. Reproduced with permission from Ref. [127] ©2024, Elsevier Ltd.

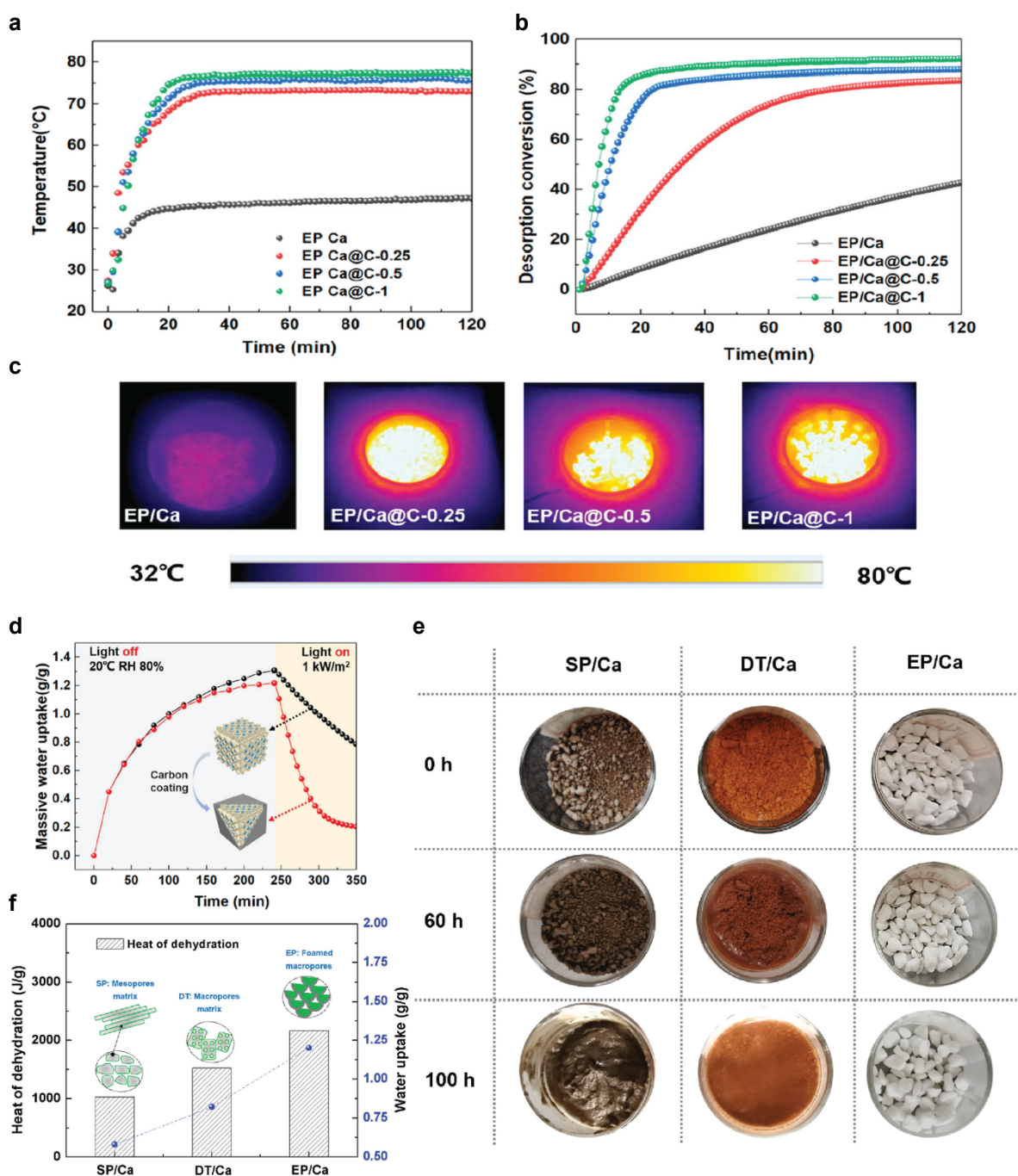


Figure 8 Sorption performance and stability of composite materials: (a) Desorption performance curve of sorbents as a function of time under a solar simulator with a solar radiation intensity of 1 kW/m²; (b) Time course of the temperature profile of sorbents during solar desorption. (c) IR image of sorbents. (d) Massive water uptake of sorbents. Reproduced under the CC BY-NC-ND 4.0 license from Ref. [126] ©2021, American Chemical Society. (e) Composite sorbents after water vapor sorption at 10°C and 73% RH. (f) Heat of dehydration for porous minerals with different structural properties. Reproduced with permission from Ref. [130] ©2024, Elsevier B.V.

high humidity levels because of capillary adsorption effects. The composites also demonstrated excellent cycling stability, with less than a 5% reduction in water uptake and less than a 15% loss in heat storage density after 20 cycles^[127].

In a similar approach, researchers impregnated a hydrothermally reduced graphene oxide aerogel with MgCl₂ hydrates to tune its pH and temperature. The resulting composite achieved a maximum water uptake of 1.16 g/g, which was enabled by its exceptionally high salt

loading of 97.3 wt%. Furthermore, the material displayed remarkable cyclic stability, retaining 95% of its initial energy storage capacity after five consecutive charge-discharge cycles^[128]. Carbon-based matrices, particularly ENG, have been shown to improve both the mechanical stability and thermal conductivity of salt hydrate composites. However, an intrinsic trade-off exists between enhanced heat transfer and reduced vapor permeability, which poses a significant design constraint for material development. Future research must therefore aim to over-

come this limitation by developing advanced material architectures and processing methods. Key strategies include surface modification of graphite flakes, integration of ENG with fibrous supports, use of innovative additives and synthesis conditions, and development of hierarchical pore topologies. To achieve balanced performance, the primary goal is to decouple and optimize the mass- and heat-transport channels while ensuring the long-term cyclic stability of the composite material.

4.4 Mineral-based composites for thermochemical heat storage

Porous minerals have high specific surface areas, high pore volumes, good mass transfer characteristics, and high storage capacities. They can be categorized into one-, two-, and three-dimensional porous mineral-based materials on the basis of their mineral carriers. Common porous minerals include EP, diatomaceous earth, sepiolite, augite, vermiculite, and others^[129]. Vermiculite, a naturally occurring group of hydrated lamellar minerals (aluminum-iron-magnesium silicates), is prized for its high pore volume, low cost, and strong water retention. It may also intercalate salt. However, serious problems can arise from the material's relatively small surface area and its tendency to change structure during cycling, leading to swelling and shrinking^[9]. Wei et al.^[130] developed inexpensive CaCl_2 -mineral composites using materials with natural pore structures. To investigate how porous architectures affect composite sorbent performance during storage cycling, researchers selected three matrix materials: sepiolite (SP) with mesopores, diatomite (DT) with macropores, and EP with foamed macropores (Figs. 8e and 8f). The foamed macropores of EP provided the greatest capacity to contain CaCl_2 , significantly outperforming the mesopores of SP and the macropores of DT. This resulted in a high salt content of 64% in the EP/Ca composite, which was noticeably higher than that in the SP/Ca and DT/Ca composites. Importantly, the EP/Ca composite exhibited no solution leakage during operation because of the capillary forces of the foam macroporous material, indicating improved structural stability. In contrast, both DT/Ca and SP/Ca experienced solution overflow after sorption. Under sorption conditions of 20°C and 80% RH, with desorption at 200°C, the performance of the composites was as follows: the average water exchange of the SP/Ca was 0.58 g/g, the ESD was 1026 J/g (114 kWh/m³), the DT/Ca was 0.82 g/g and 1520 J/g (169 kWh/m³), and the EP/Ca was 1.20 g/g and 2166 J/g (241 kWh/m³). All the composites exhibited relatively strong hydrothermal stability, maintaining their water absorption performance over repeated sorption-desorption cycles.

A composite sorbent was created by combining expanded vermiculite (EVM) and SrBr_2 for low-temperature TES (<100°C). The sorption process comprises three steps: the hydration of $\text{SrBr}_2 \cdot \text{H}_2\text{O}$ crystals, liquid-gas absorption in the SrBr_2 solution, and initial water absorption in the EVM. Despite its low adsorption capacity, the macroporous, slit-shaped structure of EVM efficiently hosts salt and prevents solution leakage in a closed system. The findings show that as the salt concentration increases, the ESD and total water intake increase. The optimal composite, EVMSrBr₂40, has a water uptake of 0.53 g/g, a

mass ESD of 0.46 kWh/kg, and a volumetric ESD of 105.36 kWh/m³. Increased water loss during desorption is offset by increased storage density, as evidenced by reaction enthalpies ranging from 41 to 70 kJ/mol of water (Figs. 9a and 9b). Overall, compared with bulk salt, the EVM/SrBr₂ composites show potential for low-temperature applications. They effectively leverage the thermally expanded, layered porosity of vermiculite to improve vapor transport and structural stability^[71].

Space heating was performed by confined K_2CO_3 with a high salt content of 69% in an enlarged vermiculite matrix. Compared with loose salt grains of the same size, the K_2CO_3 contained hydrated grains faster. After 74 cycles of hydration and dehydration, the average grain size and chemical composition of the composite were fixed, whereas its physical morphology and texture remained variable (Fig. 9c). The composite bed maintained a consistent performance for at least 47 cycles, with a high volumetric ESD of 250 kWh/m³ under working conditions that included deliquescence (Fig. 9d). This demonstrates its promise as a low-cost, long-lasting substance for low-temperature TCHS in residential areas^[131].

Sutton et al.^[132] investigated salt-in-matrix (SIM) composites for TCHS in combination with transpired solar collectors. The composites were prepared by impregnating porous vermiculite with either CaCl_2 or LiNO_3 . Although the initial results were encouraging, laboratory studies revealed a significant performance limitation: heat production decreased after 60 h of operation, and the maximum temperature increase in the reactor during discharge was only 14°C, which is far below the theoretical expectations. The primary issue was poor salt distribution within the vermiculite matrix. Moisture penetration in air was limited to approximately 100 mm, causing localized deliquescence that blocked further vapor movement and hindered complete hydration. Additionally, the salt-to-matrix ratio proved critical. A 2:1 ratio provided better structural integrity and salt distribution, whereas a 3:1 ratio led to salt accumulation and particle damage, as illustrated in Fig. 10.

The ESD of the CaCl_2 @EV composite was approximately 290 kWh/m³; however, owing to incomplete conversion, real-world values may be lower, ranging from 150 to 200 kWh/m³. For TCHS systems charged with solar thermal energy, newly developed vermiculite-salt mixtures, particularly the MgSO_4 - CaCl_2 combination, show considerable promise. These composites offer high energy density and enhanced sorption properties, potentially overcoming the high regeneration temperature challenge associated with conventional matrix zeolites. Furthermore, the ESD of an EV with mixed salts was typically higher than that of an EV with a single salt, as illustrated in Fig. 9e^[133].

4.5 MOF-based composites for thermochemical heat storage

MOFs consist of metal nodes connected by organic linkers, yielding extremely high specific surface areas, adaptable pore chemistries, and porosities exceeding 60%^[134]. These characteristics make them ideal for TCHS applications, as their large pore volumes can accommodate significant amounts of hygroscopic salts while promoting effi-

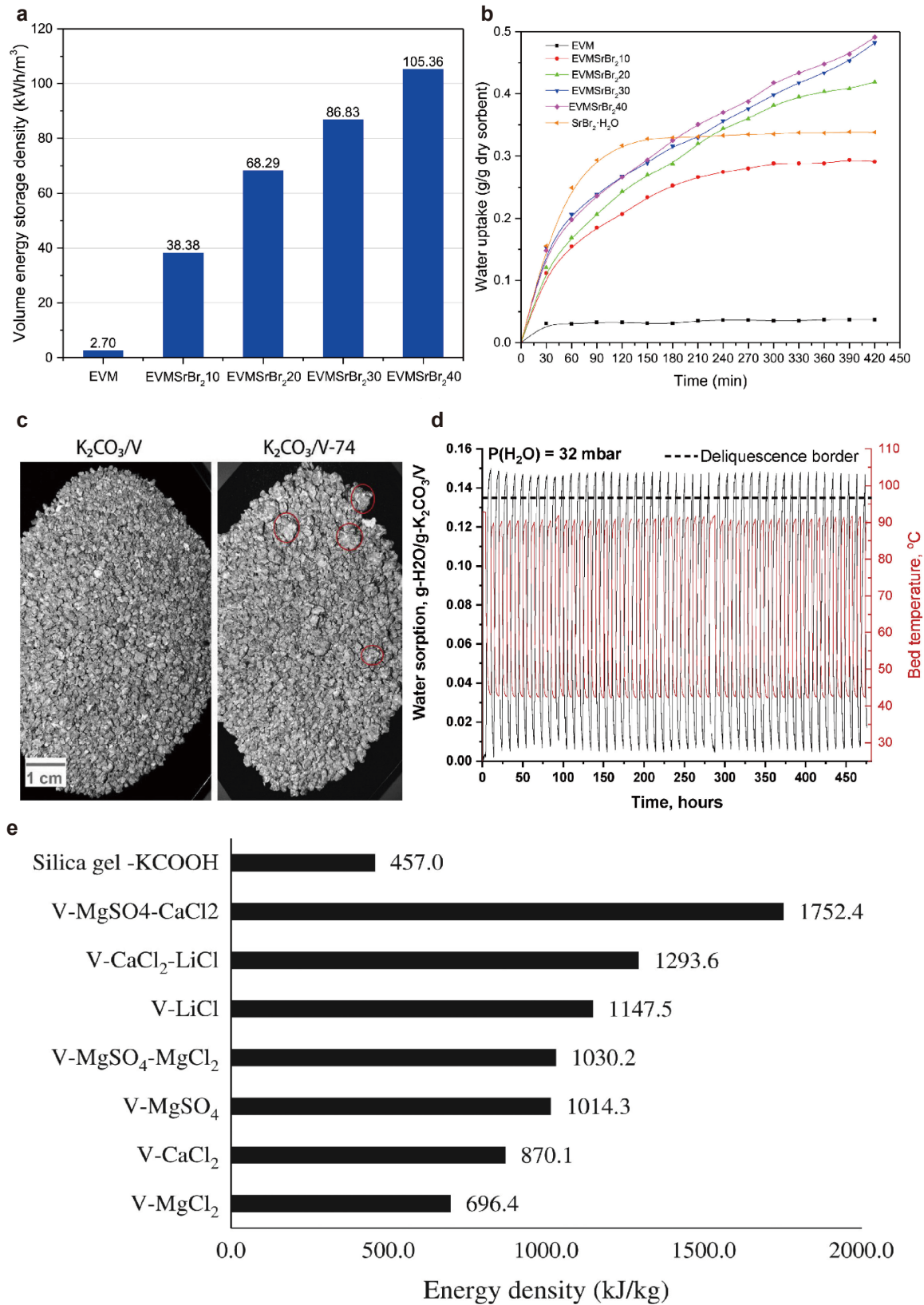


Figure 9 Performance evaluation of composite sorbents for TCHS: (a) Volumetric ESD of EVM and EVM/SrBr₂ composites. (b) Water sorption kinetics at 30°C and 60% RH for comparison of EVM, SrBr₂·H₂O, and EVM/SrBr₂. Reproduced with permission from Ref. [71] ©2016, Elsevier Ltd. (c) Photographs of the K₂CO₃/V bed before cycling and after 74 hydration–dehydration cycles. (d) Water sorption during cycling of K₂CO₃/V over 47 sorption–desorption cycles at evaporator temperature (T_e) = 25°C and a hydration temperature (T_h) = 40°C. Reproduced under the CC-BY-NC-ND license from Ref. [131] ©2019, The Authors. (e) Energy density analysis for the investigated composite materials. Reproduced under the CC-BY-NC license from Ref. [133] ©2017, The Authors.

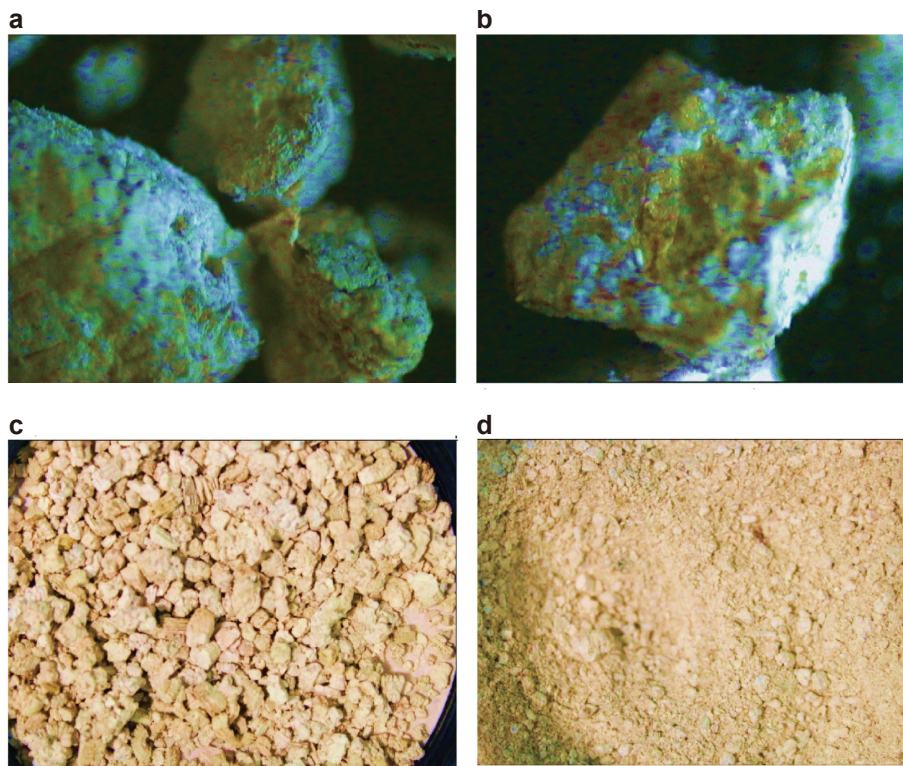


Figure 10 Morphology of CaCl_2 -vermiculite composite materials prepared with different salt-to-matrix ratios: (a) CaCl_2 :vermiculite SIM = 2:1 (image width = 6.5 mm). (b) CaCl_2 :vermiculite SIM = 3:1 (image width = 6.5 mm). (c) CaCl_2 :vermiculite SIM = 2:1 as a bulk mixture. (d) CaCl_2 :vermiculite SIM = 3:1 as a bulk mixture. Reproduced with permission from Ref. [132] ©2017, Elsevier B.V.

cient vapor flow. Research has indicated that compared with conventional sorbents and zeolites, MOFs typically exhibit superior water sorption isotherms; for instance, MIL-125(Ti)- NH_2 demonstrates a high heat storage capacity of 112.7 kWh/m^3 ^[134,135]. Furthermore, using MOFs as the porous matrix for salt composites significantly reduces salt agglomeration and deliquescence, thereby enhancing the stability and performance of the composite material^[134].

Sun et al.^[136] used the wet impregnation method to incorporate LiCl into the microporous metal-MOF UiO-66, producing LiCl@UiO-66 , a high-performance composite adsorbent for adsorptive heat transformation. This approach yielded a genuine salt-in-MOF composite with significantly enhanced water absorption and no signs of salt deliquescence. In particular, the 30% LiCl composite, LiCl@UiO-66-30 , exhibited a remarkable water uptake of more than 2.15 g/g at relatively high pressure ($p/p_0 = 0.9$). This value surpasses that of all known UiO-66-based composites and is three to eight times greater than that of pure UiO-66. Cycling tests confirmed the hydrothermal stability of the material. Although its sorption kinetics were slightly slower than those of neat UiO-66, they remained faster than those of conventional salt-in-silica gel composites were. The LiCl@UiO-66-30 composite achieved a high coefficient of performance of 1.64 for heat pumping and a significant heat storage capacity of 900 kJ/kg ($\sim 150 \text{ kWh/m}^3$). This performance exceeded that of comparable composites, such as $\text{CaCl}_2\text{@UiO-66}$, suggesting that a substantial energy-storage goal could be achieved with just 10 kg of material. This achievement highlights the primary advantage of employing MOFs as host materials: their properties can be precisely tailored

through functionalization to maximize hydrophilicity and optimize overall system performance.

Researchers developed a method to improve the efficiency of CaCl_2 in TCHS by using functionalized MOFs as porous host matrices. In one study, CaCl_2 was incorporated into MIL-101(Cr) frameworks bearing various functional groups, including amino (NH_2), sulfonic acid (SO_3H), hydrogen (H), methyl (CH_3), and fluorine (F), to produce a range of composites. The findings showed that performance is directly influenced by changes in the hydrophilicity of the MOF. Among the composites tested, the sulfonic acid-functionalized MOF, designated MIL-101(Cr)- $\text{SO}_3\text{H}/\text{CaCl}_2$, exhibited the highest performance, achieving a heat storage density of 1274 J/g ($\sim 159 \text{ kWh/m}^3$) and the greatest water sorption capacity of 0.6 g of water per gram of sample. Furthermore, all the composites in the series demonstrated outstanding cyclic stability over 17 consecutive adsorption-desorption cycles, with only a minimal decrease of 6.8% in the ESD and minimal performance degradation^[137].

Yang et al.^[138] developed a lithium hydroxide (LiOH) composite for TCHS using a porous carbon matrix (ZSPCM) derived from carbonized ZIF-8 at 700°C . The resulting matrix had a high surface area of $890.2 \text{ m}^2/\text{g}$, facilitating the dispersion of small LiOH particles and improving water adsorption kinetics and vapor-molecule contact. The hybrid composite containing 50% LiOH, designated Li/ZSPCM-50, exhibited several advantages over pure LiOH, including a high heat storage density of 1373.3 kJ/kg ($\sim 229 \text{ kWh/m}^3$), enhanced water sorption capacity, a low charging temperature, and excellent thermal conductivity (Fig. 11a). Compared with pure LiOH,

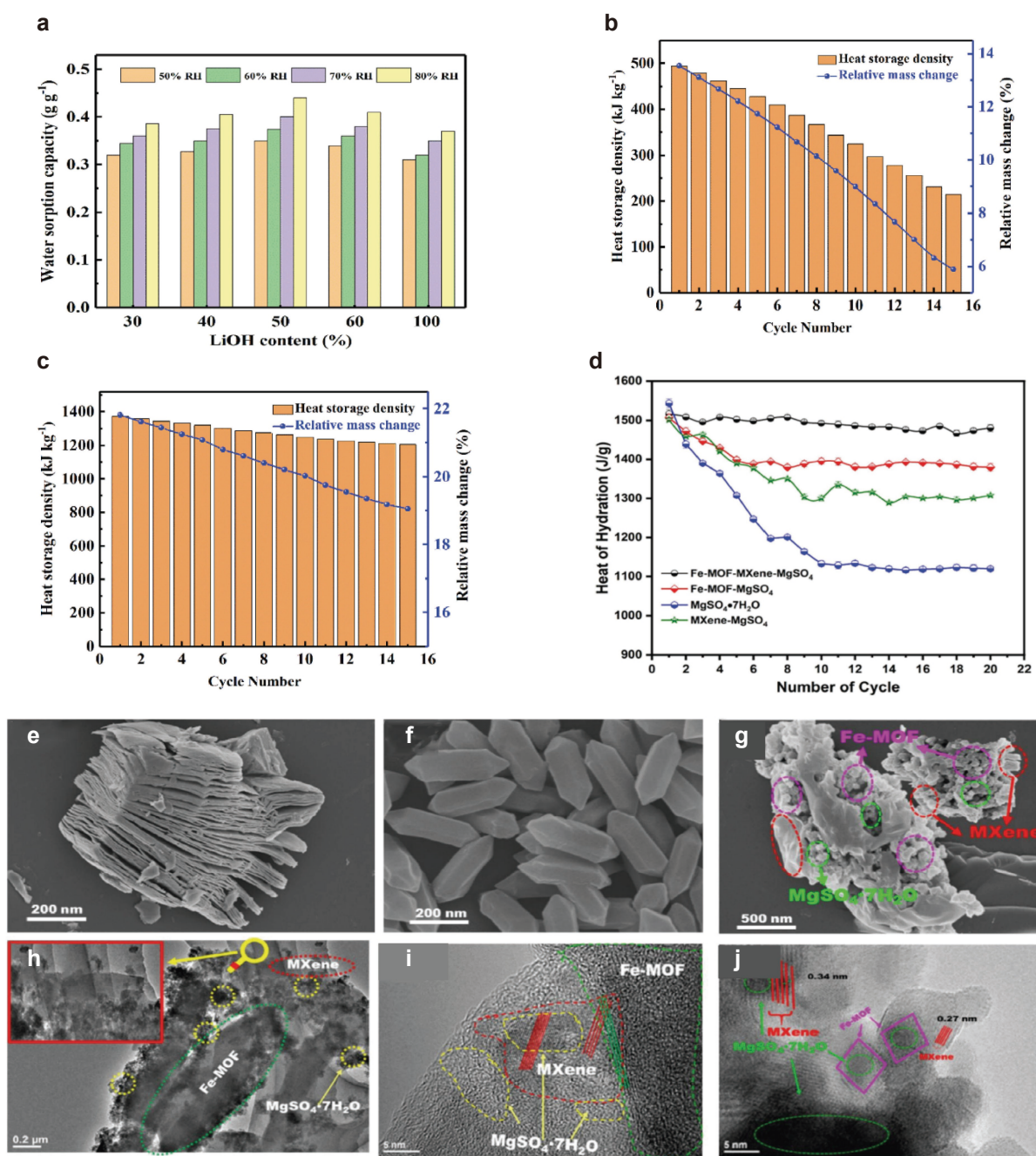


Figure 11 Advanced composite sorbents for TCES: (a) Water adsorption capacity of pristine LiOH and Li/ZSPCM(700)-X composites with varying LiOH contents at 30°C under different RH levels. Cycling performance and dehydration activation energy of pristine LiOH (b) and Li/ZSPCM(700)-50 composite (c). Li/ZSPCM(700)-X refers to LiOH-loaded ZSPCM (700) composites, where ZSPCM(700) is the support material calcined at 700 °C and X represents the LiOH loading (wt.%). Reproduced with permission from Ref. [138] ©2021, Elsevier Inc. (d) Recyclability comparison of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, MXene- MgSO_4 , Fe-MOF- MgSO_4 , and Fe-MOF-MXene- MgSO_4 composites. (e–j) Microstructural characterization showing SEM images of MXene (e), Fe-MOF (f), and Fe-MOF-MXene- MgSO_4 (g); TEM inset of MXene (h); and HRTEM images of Fe-MOF-MXene- MgSO_4 (i–j) revealing the composite morphology and interfacial features. Reproduced with permission from Ref. [68] ©2025, Elsevier Ltd.

the composite also showed remarkable cyclic stability, maintaining a significantly better performance, which deteriorated by 56.5% over 15 cycles (Figs. 11b and 11c). However, the study identified a critical design limitation: high salt loading, specifically 60% LiOH, reduced the sorption performance because of pore blocking and surface accumulation, highlighting a universal challenge in composite material design.

According to Rehman et al.^[68], a Fe-MOF-MXene- MgSO_4 composite outperformed pure $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in TCHS. With a high hydration enthalpy of 1503 J/g (~251 kWh/m³), the composite outperforms the pure salt by 1180 J/g (~197 kWh/m³). It showed remarkable cycling stability, with only a 2.08% loss of its capacity after 20 consecutive cycles of hydration and dehydration, compared with the 24.27% loss of pure salt (Fig. 11d). This

stability is attributed to a synergistic effect; the Fe-MOF prevents salt aggregation, and the MXene provides structural integrity, as evidenced by the uniform dispersion of components, as illustrated in Figs. 11e–11j. One significant improvement was a 522% increase in thermal conductivity to 2.24 W/(m·K), which was attributed to the integrated conductive MXene framework. High salt concentrations increase the energy density but significantly affect the essential pore properties (size, volume, and surface area) and the kinetics of adsorption and desorption of the composite. Therefore, enhancing overall performance requires optimizing the salt concentration.

Other studies have achieved high salt loadings when SrBr₂ is encapsulated in the mesoporous MOF MIL-101(Cr). Owing to both a high salt loading of 63 wt% and unexpected beneficial changes in the water sorption behavior of the salt confined within the MOF pores, the composite achieved an extraordinary volumetric heat storage density of 233 kWh/m³, allowing for effective operation at a low vapor pressure of 1.25 kPa. Cyclic stability tests were conducted under actual seasonal storage conditions (1.25 kPa, 30–80°C). The overall water uptake decreased by 14.1% after 10 full cycles. Interestingly, the first five cycles accounted for the majority of this degradation (9.5%), after which the rate of capacity loss immediately decreased, suggesting effective material stabilization^[100].

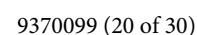
In a separate development, researchers synthesized alkylated meso-macroporous Cr-MIL-101 hollow tubes, abbreviated as ACHT, by coordinating chromium ions (Cr³⁺) with alkylated bridged ligands (Fig. 12a)^[134]. These hollow tubes have a broad pore diameter of 5–136 nm and a relatively high thermal storage capacity of 187 J/g (46.7 kWh/m³). When combined with octadecane to form form-stable phase change materials, the resulting octadecane@ACHT composites show promise for practical applications, including integration into building interior walls to improve indoor thermal comfort or incorporation into thermally regulated textiles and clothing^[139]. Researchers developed an advanced TCHS materials by modifying an aluminum-based metal-MOF as a solid adsorbent. The initial matrix, designated Al-Fum-Al₂O₃, was prepared by incorporating nanoaluminum oxide (nano-Al₂O₃) into the aluminum fumarate MOF structure. The final composite, LiCl@Al-Fum-Al₂O₃, was synthesized by encapsulating LiCl within the modified matrix via wet impregnation. At an optimal aluminum oxide mass fraction of 13%, the thermal conductivity of the composite was 0.21448 W/(m·K), which is a substantial 66% improvement over that of pure Al-Fum. More significantly, the encapsulation of LiCl within the pore structure of Al-Fum-Al₂O₃ led to a remarkable increase in TCHS performance. The heat of adsorption ranged from 1185.22 kJ/kg (198 kWh/m³), an 85% increase relative to that of the unmodified Al-Fum-Al₂O₃ matrix. The durability of the material was confirmed through extended cycling tests, as illustrated in Figs. 12b–12e. After 20 consecutive adsorption-desorption cycles, the composite maintained stable adsorption-desorption kinetics with only minimal fluctuations in heat storage capacity. The thermal conductivity enhancement was well maintained throughout the cycling process, and the positive impact of nano-Al₂O₃ on water adsorption

performance remained consistent. These results collectively demonstrate that incorporating nano-Al₂O₃ into the MOF matrix, combined with LiCl encapsulation, yields a composite with superior thermal properties, enhanced heat storage capacity, and excellent cycling stability^[140].

The poor intrinsic thermal conductivity of pristine MOFs (e.g., 0.17 W/(m·K) for ZIF-8 and 0.31 W/(m·K) for MOF-5) can impede heat transfer rates during sorption-desorption cycles, despite their other benefits^[141,142]. Ali et al.^[143] produced a low-cost Ti₃C₂ MXene-MOF composite (TMX-MOF) for TES using recovered carbon soot and aluminum. The performance of the composite greatly improved when it was combined with paraffin wax; a 0.5 wt% loading increased the thermal conductivity by 40%, enhanced the thermal stability, and resulted in a high photothermal conversion efficiency of 86.3%, indicating strong potential for sustainable heat management (Fig. 13a). Composites with high-thermal-conductivity additives are being developed as a solution. Strategies such as (1) encapsulation with expanded graphite (EG)-composites containing 0–10% w/w EG have demonstrated a fivefold increase in thermal conductivity^[144], and (2) *in situ* growth with a PEG@CNTs/Cr-MIL-101-NH₂ composite produced by *in situ* growth increased the thermal conductivity by more than 100% and resulted in a large phase-change enthalpy, good chemical stability, and excellent thermal cycling stability (Figs. 13b–13e)^[144]. As shown in Fig. 13f, N-doped porous carbon (NPC-Al), synthesized using a one-step process with NH₂-MIL-53(Al) (a MOF), was used to prepare a polyethylene glycol (PEG)-based composite. NPC-Al exhibited large and regular pore dimensions and a large specific surface area (2193.5 m²/g), providing a way to combine customized porosity with enhanced conductivity^[101].

MOFs, particularly those belonging to the Materials of Institute Lavoisier (MIL), University of Oslo (UiO), and Zeolitic Imidazolate Frameworks (ZIFs) families, provide a versatile platform for the development of high-performance composite sorbents for TCHS. As summarized in Table 3, MOF-based composites generally exhibit superior energy storage density, high porosity, and excellent tunability compared with many conventional porous supports, although challenges related to thermal conductivity, cost, and large-scale implementation remain. Looking ahead, future research should move beyond these widely investigated MOF families to explore alternative framework structures and systematically examine how key parameters, including MOF particle size, pore architecture, and surface functionalization, influence long-term stability, salt dispersion uniformity, and vapor diffusion kinetics within the composites. Furthermore, to bridge the gap between laboratory-scale materials and practical applications, it is essential to integrate MOFs with thermal conductivity enhancers. Such an approach will facilitate the development of next-generation composite sorbents that simultaneously achieve high energy storage density and enhanced power density, thereby meeting the demanding performance requirements of practical TCHS systems.

Overall, the diverse families of composite materials developed for TCHS each offer distinct advantages and limitations, and no single material currently satisfies all the



requirements for practical applications. Consequently, the optimal material selection depends on the specific performance priorities of the intended application. Carbon-based composites are preferred for high power density and rapid heat and mass transfer, silica-based composites provide excellent structural stability and cycling durability,

zeolite-based composites are particularly suitable for low-temperature heat storage owing to their strong water adsorption characteristics, MOF-based composites achieve the highest thermochemical energy storage densities because of their exceptional porosity and tunable structures, while naturally occurring mineral-based composites

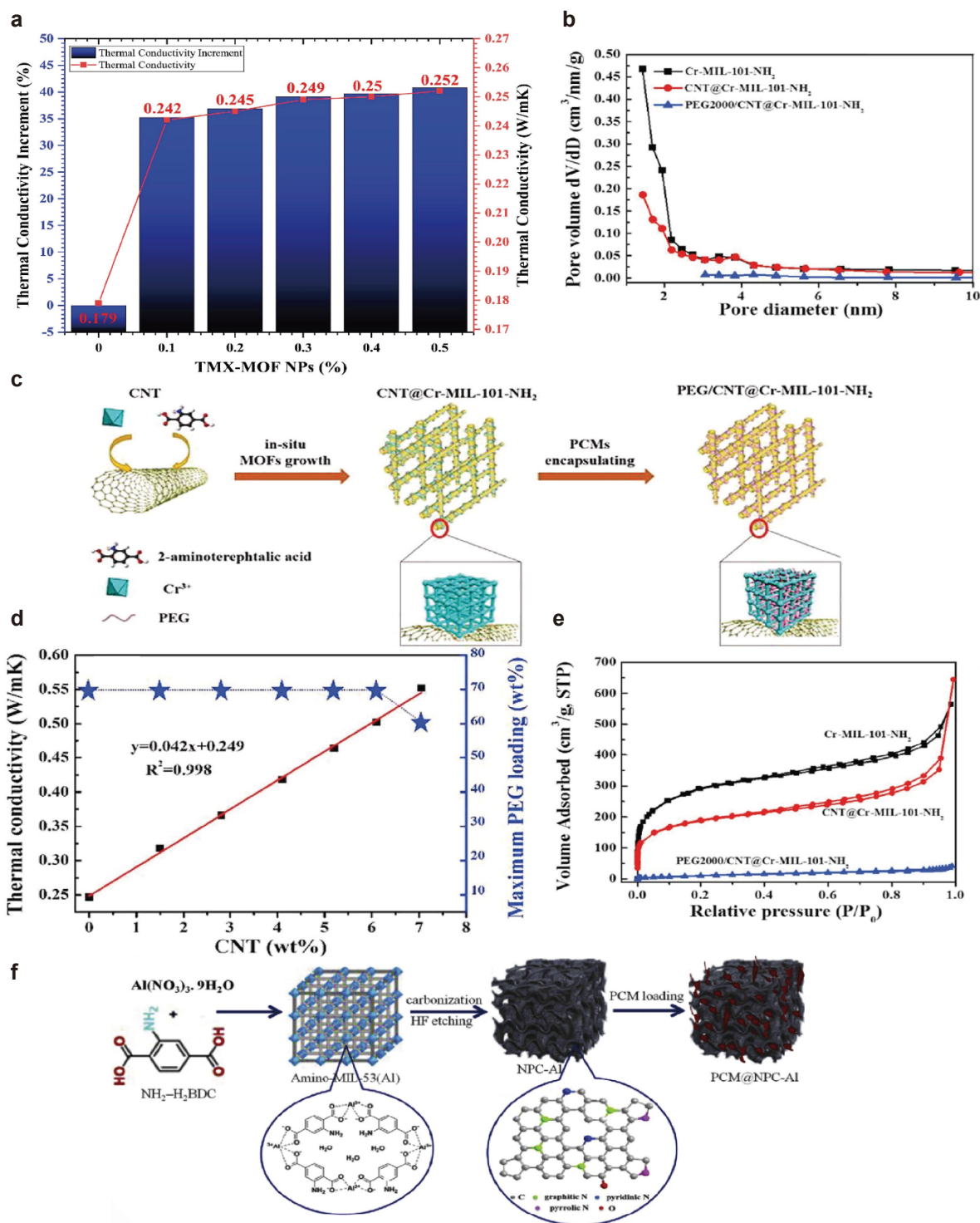


Figure 13 Synthesis and characterization of MOF-based phase change composites: (a) Thermal conductivity comparison of pure paraffin wax and TMX-MOF-modified phase change composite. Reproduced with permission from Ref. [143] ©2025, Elsevier Ltd. (b) Pore size distributions of the Cr-MIL-101-NH₂, CNT@Cr-MIL-101-NH₂ hybrid composite, and PEG2000/CNT@Cr-MIL-101-NH₂ PCM composite. (c) Schematic illustration of the synthesis of the PEG/CNT@Cr-MIL-101-NH₂ PCM composite. (d) Thermal conductivity of composites with varying CNT mass percentages. (e) N₂ adsorption-desorption isotherms of the Cr-MIL-101-NH₂, CNT@Cr-MIL-101-NH₂ hybrid, and PEG2000/CNT@Cr-MIL-101-NH₂ PCM composite. Reproduced with permission from Ref. [144] ©2018, Elsevier B.V. (f) Schematic illustration of PEG@NPC-Al composite synthesis. Reproduced with permission from Ref. [101] ©2019, Published by Elsevier Ltd.

offer a cost-effective and scalable solution for large-scale thermal energy storage systems. Therefore, selecting an appropriate composite family requires balancing energy

storage capacity, thermal conductivity, cycling stability, operating temperature, and economic feasibility according to the target application.

Table 3 Summary of the research on composite materials for TCES.

Matrix	salt	Salt content (wt%)	Exp. energy storage capacity, (kWh/m ³)	Adsorption temperature (°C)	Desorption temperature (°C)	Adsorption pressure (mbar)	Refs.
Expanded graphite	CaCl ₂	62–63	~135–278	20	150	~40%RH	[145]
Expanded vermiculite	K ₂ CO ₃	69	~ 250	40	120	22–117	[131]
Expanded graphite	MgSO ₄	60	199.6	25	–	~85%RH	[70]
Silica gel	SrBr ₂	58	~ 203	30	80	12.5	[77]
Silica gel	CaCl ₂	43	~211.1	30	80	12.5	[78]
Silica gel	CaCl ₂	15	207.2	20	150	7	[89]
Alumina	CaCl ₂	15	160.0	20	150	7	[89]
Silica-PEG	CaCl ₂	32–42	217.2	30	130	~42%RH	[146]
Silicone foam	MgSO ₄	40–70	–	–	150	23.4	[119]
Activated carbon	MgSO ₄	30	366.7	30	150	~60%RH	[147]
Bead-activated carbon	MgSO ₄	7.6	255.6	30	150	~60%RH	[148]
Carbon Nanotubes	CaCl ₂	53	147.0	35	75	8.7	[69]
Carbon Nanotubes	LiCl	44	470.0	35	75	8.7	[69]
Cement	SrCl ₂	50	~136	–	<90	–	[149]
Diatomite	MgSO ₄	60	214.7	25	250	~85%RH	[90]
Bentonite	CaCl ₂	15	199.7	20	150	7	[89]
Hydroxyapatite	MgSO ₄	20	128.9	30	150	~60%RH	[150]
Zeolite 13X	MgSO ₄	15	180.0	25	150	15.8	[85]
MIL-101(Cr)	Na ₂ S ₂ O ₃	61.8	305.4	30	120	12.7	[151]
MIL-101(Cr)	SrBr ₂	63	~ 233	30	80	12.5	[152]
MIL-101(Cr)	SrBr ₂	63	375.0	30	80	12.5	[100]
MIL-100(Fe)	CaCl ₂	46	376 ^a /334 ^b	30	80	12.5	[153]
MIL-101(Cr)-NH ₂	CaCl ₂	45	335 ^a /313 ^b	30	120	13.5	[137]
MIL-101(Cr)	CaCl ₂	62	485 ^a /446 ^b	30	80	12.5	[153]
MIL-101(Cr)	CaCl ₂	46.7	311 ^a /286 ^b	30	120	13.5	[137]
MIL-101(Cr)-SO ₃ H	CaCl ₂	43.1	354 ^a /311 ^b	30	120	13.5	[137]
MXene	MgCl ₂	86–97	618.6	–	–	~85%RH	[154]

Note: a, energy storage capacity of the first adsorption-desorption cycle; b, energy storage capacity of the *n*th adsorption-desorption cycle.

5 Mixed-salt composites for thermochemical heat storage

Mixed-salt systems, typically composed of binary salt combinations, offer another promising approach to enhance the performance of TCES systems. Although single-salt hydrates have been extensively studied, they often exhibit inherent limitations, including deliquescence, low energy density, and restricted operating temperature ranges. These challenges can often be mitigated by combining salts to form mixed-salt composites. The incorporation of multiple salts can improve the hydration and dehydration behavior, alter the thermodynamic characteristics, and enhance the cycling stability compared with their single-salt counterparts. This section provides a comprehensive overview of mixed-salt systems, including the typical salt pairings examined in the literature. The significant impact of salt pairing on key TCES performance metrics, including ESD, operating temperature range, sorption kinetics, and long-term cyclic durability, is discussed.

For instance, to achieve advantageous performance, a

hydrothermally stable salt with a high deliquescence RH and a small amount of deliquescence salt was combined. The combined sulfate-chloride system was the most notable illustration of this phenomenon. Because of its considerable hygroscopicity and tendency to overhydrate, which slows the reaction, chloride considerably decreases the stability of the hydration process. Another is that sulfate has poor reaction kinetics, ineffective water vapor transfer, and an inadequate reaction to the effects of salt pairing on critical TCES performance and metabolism^[61]. Strategically combining sulfate and chloride salts into binary mixtures offers an effective way to overcome the individual limitations of each component in thermochemical hydration reactions^[155]. When these salts are mixed, the dehydrated sulfate partially dissolves in the solution of the hydrated salt, resulting in the formation of a higher hydrated state. This interaction yields two key benefits: it improves the sulfate salt's hydration kinetics while preventing the instability typically caused by excessive chloride hydration. However, to prevent chloride-induced corrosion of the reactor, the mixture must be formulated with a high sulfate ratio and a low desorption temperature^[66]. This well-rounded strategy minimizes the disad-

vantages of each salt type while leveraging its advantages.

Binary salt mixtures of SrCl_2 and MgCl_2 were prepared by ball milling and screening until the particles were uniformly smaller than 50 μm . To overcome the metastability constraints of SrCl_2 , highly hygroscopic and deliquescent MgCl_2 was deliberately added to this formulation to improve the overall reaction kinetics. This performance enhancement is hypothesized to result from the formation of a wetting layer and the associated change in enthalpy during dissolution. Notably, because both salts share a common chloride ion, the mixtures interact only physically, minimizing the likelihood of undesirable side reactions or the formation of new chemical compounds. The binary $\text{SrCl}_2/\text{MgCl}_2$ mixture outperformed its constituent salts in terms of operational adaptability across a broader RH range of 25% to 60% at 25°C, with MgCl_2 operating below 30% and SrCl_2 above 60%. As shown in Figs. 14a and 14b, a 50/50 mass mixture demonstrated an impressive energy storage capacity of more than 1100 J/g ($\sim 367 \text{ kWh/m}^3$), which remained at 80% of the initial value for 20 consecutive cycles. Additionally, Fig. 14c implies that the fundamental mechanism highlights the primary advantage of mixing two salts with different phase behaviors: achieving full hydration while avoiding complete deliquescence^[156].

The composites use EV as the host matrix, which is impregnated with binary and ternary salt mixtures, including $\text{MgSO}_4\text{-CaCl}_2$, $\text{MgCl}_2\text{-LiNO}_3$, $\text{MgSO}_4\text{-LiCl}$, and $\text{MgSO}_4\text{-LiNO}_3\text{-MgCl}_2$, as illustrated in Fig. 14d. Among these formulations, vermiculite impregnated with the binary $\text{MgSO}_4\text{-CaCl}_2$ mixture showed exceptional performance, with a high volumetric energy storage density of 1213 kJ/kg ($\sim 169 \text{ kWh/m}^3$) and fast desorption kinetics across the temperature range relevant to low-grade heat applications. A comparative analysis of moisture sorption capacity is shown in Fig. 14e, which reveals that the V- $\text{CaCl}_2\text{-MgSO}_4$ composite achieved the highest water uptake, 0.42 g/g, after 20 hours. This outstanding performance indicates excellent suitability for domestic TCHS applications, particularly for space heating. Furthermore, the composite demonstrated stable cyclic performance over 20 consecutive charge-discharge cycles, maintaining approximately 91.3% of its initial ESD, confirming its long-term operational reliability^[157].

The data in Fig. 14f imply that researchers prepared binary hydrated salt composites of SrCl_2 and CaCl_2 by impregnating EP, a porous carrier. The results revealed a significant synergistic effect between the two salts, with CaCl_2 enhancing the hydration behavior of SrCl_2 . When the $\text{SrCl}_2\text{-to-CaCl}_2$ mass ratio exceeds 1:1, this synergy substantially improves the overall performance of the binary-salt composites, yielding superior thermal storage performance and cycling stability compared with those of the mono-salt composites. Specifically, the optimal formulation was achieved at a $\text{SrCl}_2\text{-to-CaCl}_2$ mass ratio of 2:1 with a salt impregnation concentration of 30%. Under these conditions, the composite exhibited exceptional thermal storage performance, reaching a maximum adsorption capacity of 1.06 g/g at 20°C and 80% RH. This corresponds to a heat storage density of 1273 kJ/kg ($\sim 177 \text{ kWh/m}^3$), representing remarkable improvements of 82.76% and 47.17% over those of the SrCl_2 mono-salt

adsorbent under identical conditions (Fig. 14g). Furthermore, the optimized composite exhibited minimal deliquescence and reduced agglomeration. It decreased structural damage during cycling, thereby demonstrating the strongest cycling stability among the formulations tested^[103].

A binary hydrated $\text{MgCl}_2\text{-CaCl}_2$ salt was composited with zeolite. The optimal formulation was a total salt concentration of 15 wt%, corresponding to a 1:1.5 mass ratio of MgCl_2 to CaCl_2 . During energy discharge, the temperature of the composite increased by 45.8°C at an air velocity of 0.18 m/s. The maximum volumetric ESD reached 136 kWh/m³, with a 41.9% thermal efficiency at 0.32 m/s. Integrating metal mesh nets further enhanced performance: the temperature rise peaked at 52.7°C, the storage density was 174 kWh/m³, and the thermal efficiency was 46.1%^[158].

In another important study, Posern et al.^[155] examined the effects of the salt-content ratio in a composite comprising MgSO_4 , MgCl_2 , and attapulgite, which serves as a porous matrix. The system performed well. The components in this system have different DRH values: 90% for MgSO_4 and 33% for MgCl_2 at 30°C. According to their findings, a higher heat of sorption was observed for MgSO_4 and MgCl_2 because of increased water absorption in the MgCl_2 solution. In dehydration experiments at 130°C, a mixture of 20% MgSO_4 and 80% MgCl_2 embedded in attapulgite resulted in a measured heat of sorption of 1590 kJ/kg at 30°C and 85% RH. Similarly, Rammelberg et al.^[159] enhanced the concept by creating three binary combinations of MgSO_4 , MgCl_2 , and CaCl_2 salt hydrates. Compared with their pure constituents, all three mixed compounds showed improved cycling performance, as determined by experiments conducted at a constant vapor pressure of 21 mbar. After 55 cycles, the $\text{CaCl}_2/\text{MgCl}_2$ mixture showed excellent stability. Additionally, Ejeian et al.^[160] prepared MgSO_4 -based composites with LiCl and activated carbon fibers, using MgSO_4 specifically to reduce solution leakage from overhydration and to increase the composite's adsorption capacity and mass-transfer capability. Zbair et al.^[161] created a $\text{MgSO}_4/\text{MgCl}_2$ binary system embedded in porous carbon that has kinetic advantages over mono-salt MgSO_4 , including faster hydration and higher water sorption, as MgCl_2 promotes water vapor migration and alters MgSO_4 hydration. Compared with mono-salt composites, mono-salt (MgSO_4) or binary salt ($\text{MgSO}_4\text{-MgCl}_2$) composites exhibit faster hydration kinetics and higher water adsorption capacity. The inclusion of MgCl_2 mitigates the kinetic disadvantages arising from salt aggregation and the hydrophobicity of the support. The porous carbon (PC)-60 binary composite has a water uptake of 0.75 g/g, exceeding that of PC 60 MgSO_4 (0.48 g/g). Additionally, the amount of heat produced by the composites followed a trend comparable to that of water sorption. The PC-60 MgSO_4 composite releases 52% of the heat produced by pure MgSO_4 , whereas the PC-60 binary composite releases 70% of the heat from the pure mixed salts, demonstrating the clear performance advantage of the binary salt formulation. This technology has advanced research in real-world TCES systems based on binary salts confined within porous matrices, determining the maximum salt loading and the optimal salt mixing

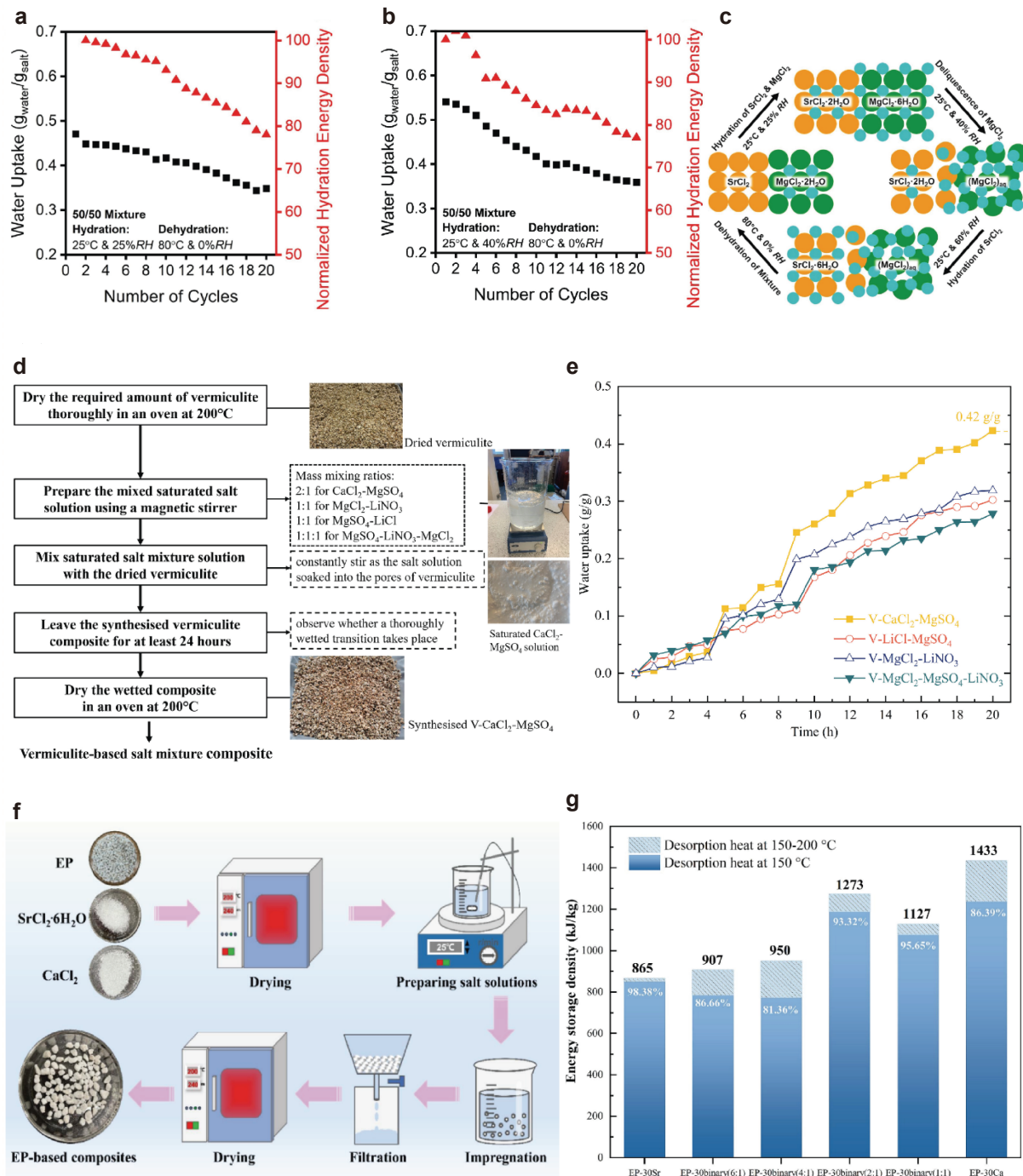


Figure 14 Synthesis, performance, and mechanisms of composite and binary salt thermochemical materials: (a) Water uptake and hydration energy density over 20 cycles for 50/50 mixtures at 25°C and 25% RH (1.5 h reaction time) and 40% RH (3 h reaction time). (b) Combined features of SrCl_2 and MgCl_2 in a 50/50 mixture at 40% RH and 25°C. (c) Mechanism illustration of binary salt mixtures, solid-gas reaction enthalpy, and MgCl_2 dissolution enthalpy promoting SrCl_2 hydration. Reproduced with permission from Ref. [156] ©2024, Elsevier Ltd. (d) Fabrication procedure of vermiculite-based salt mixture composites. (e) Water uptake variations in four composites. Reproduced under the CC BY license from Ref. [157] ©2023, The Authors. (f) Fabrication process of EP-based composites. (g) Heat storage density of EP-based composites. Reproduced with permission from Ref. [103] ©2025, Elsevier Ltd.

ratio under specific reactor operating conditions remains a critical design criterion. Furthermore, a comprehensive evaluation of the effects of process parameters on the physicochemical properties and long-term performance of the composite materials is essential. As summarized in

Table 4, mixed-salt composite materials have demonstrated significant potential for enhancing energy storage density, hydration/dehydration kinetics, and cycling stability. Nevertheless, to overcome the challenges associated with practical implementation, future research should

Table 4 Summary of mixed salt composites for thermochemical heat storage applications.

Matrix	Salt mixture	ESD (kJ/kg)	Desorption temp. (°C)	Adsorption temp. (°C)	RH (%)	Refs.
Perlite	SrCl ₂ :CaCl ₂ =2:1	1273	200	20	80	[103]
PC	MgSO ₄ :MgCl ₂ = 4:1	1840	150	30	60	[161]
Zeolite	MgSO ₄ :LiCl ₂ = 2:1	458.3	300	25	60	[162]
Vermiculite	MgSO ₄ :CaCl ₂ = 1:2	1213	150	17–19	70–80	[157]
Zeolite	MgCl ₂ :CaCl ₂ =1:1.5	714.4	250	15–20	90	[158]

extend beyond material optimization and focus on addressing reactor-scale integration, heat and mass transfer, system design, and overall engineering considerations.

6 Conclusion and future remarks

The TES will play a significant role in future net-zero carbon energy systems. Compared with SHS and LHS, TCES offers several advantages, including higher energy density, lower storage temperatures, long-term storage capability without thermal loss, environmental friendliness, and excellent cycling stability. While SHS and LHS suffer from heat loss over time and lower storage densities, TCES stores energy through reversible chemical reactions, enabling nearly loss-free storage for extended periods. This makes TCES an efficient, eco-friendly, and stable solution for TES. However, with targeted innovation and concerted research efforts, TCES systems have the potential to contribute significantly to the energy transition. The use of salt hydrates offers high energy densities and long-term stability for TCES applications. Composite materials that integrate thermal conductivity enhancers and mechanical strength significantly improve performance. Furthermore, combining different salt hydrates to form mixed salts yields synergistic effects, enhances the sorption kinetics, and increases the overall water uptake capacity. Future research on TCHS using hydrated salts should focus on the following priorities:

a) **New materials and multiscale architectures.** Research should explore novel hydrated salts beyond traditional salt hydrates and MOF families, engineer hierarchical composite architectures at multiple scales, elucidate molecular interactions between mixed salts and porous matrices, and assess long-term durability using accelerated aging techniques.

b) **Stability and performance enhancement.** Further research is needed to mitigate deliquescence, agglomeration, and caking in salt hydrates through robust composite structures with optimized porous matrices and binders. These structures must maintain mechanical integrity and prevent salt leakage during cycling. Materials degradation, thermal stability, and operational efficiency should be evaluated under realistic conditions in the long term.

c) **Energy density and cycle stability.** Improved heat storage density and thermal stability can be achieved by developing novel hydrated salts, while porous matrix composites enhance cycling stability. Precise process control during cycling extends the salt service life and improves the overall system efficiency.

d) **Heat and mass transfer enhancement.** Future efforts should improve the thermal conductivity and slow kinetics of salt hydrates. Tailored pore structure design combining macropores, mesopores, and micropores ensures

seamless transition from bulk transport to reaction sites. Optimizing composite material design and investigating mass-transfer enhancement methods will be critical to improving transport efficiency and adsorption capacity. Surface functionalization with hydrophilic groups such as hydroxyl (–OH), amino (–NH₂), or carboxyl (–COOH) groups strengthens interactions with water molecules. Additionally, materials such as MOFs and carbon-based composites are expected to increase the adsorption kinetics and thermal conductivity.

e) **Cost-effective alternatives.** Future TCES research should prioritize large-scale testing of low-cost, abundant salt composites, including MgCl₂, CaCl₂, vermiculite, and binary salt systems. Technoeconomic analysis is essential for balancing performance and economic viability.

f) **Reactor design and simulation.** Beyond material selection, reactor design and thermochemical and kinetic analyses should be conducted using analytical calculations and software simulations to optimize system-level performance.

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None.

Author contribution statement

Alemayehu Worku Sewhunegn: Writing - original draft, Conceptualization, Writing-review & editing, Investigation, Methodology. Kejian Wang: Writing - review & editing, Supervision. Mulugeta Tadesse Wotango: Writing - review & editing. Tassew Belete Bahru: Writing - review & editing. Minable Endaye Rass: Writing - review & editing. Yong Liu: Supervision, Writing - review & editing. All the authors have approved the final manuscript.

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Declaration of competing interests

There are no conflicts to declare.

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