Porous Monolithic Perovskite Structures for High-Temperature Thermochemical Heat Storage in Concentrated Solar Power (CSP) Plants and Renewable Electrification of Industrial Processes

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Abstract. A novel approach towards thermal energy storage of surplus renewable energy (RE) is introduced via a hybrid thermochemical/sensible heat storage concept implemented with the aid of porous structures made of redox metal oxides, capable of reversible reduction/oxidation upon heating/cooling in direct contact with air, accompanied, respectively, by endothermic/exothermic heat effects and demonstrating fully reversible dimensional changes under cyclic operation. The proposed modular storage units can be heated during the day to a level exceeding the metal oxide's reduction onset temperature either by hot air streams from air-operated Concentrated Solar Power (CSP) tower plants or via surplus/cheap RE-electricity from photovoltaics, wind, or other renewable sources ("charging"/energy storage step). When this RE sources become non-available or upon demand, the fully charged system can transfer its energy to a controlled airflow that passes through the porous oxide block and initiates the exothermic oxidation of the reduced metal oxide. Thus, a hot air stream is produced which can be used to provide electricity or exploitable heat for industrial processes. The present work elaborates on the operating principles and the potential application of this concept and reports progress in the preparation and shaping of reticulated porous ceramics (RPCs also known as "ceramic foams") from $CaMnO_3$-based perovskite compositions and their preliminary testing with respect to cyclic reduction-oxidation.

Keywords: Thermochemical Energy Storage, Porous Ceramics, Perovskites

1. Introduction

Dispatchable power plants can provide electricity depending on the particular demand by adjusting their power output and being turned on and off. Conventional fossil fuel power plants are dispatchable but produce pollutants including CO_2. Photovoltaics (PV) convert solar energy directly to electrical power that needs to be supplied immediately to the grid, whereas the excess electricity produced during on-sun operation needs to be stored in a multi-Megawatt Battery Energy Storage System (BESS) to be released into the grid when sun is not available; such storage systems with long-term operational reliability and competitive costs are not yet commercially available. On the contrary, Concentrated Solar Power (CSP) Plants convert solar energy to medium- to high-temperature heat and via a power cycle to electricity. Heat can be stored at a much lower cost relative to that of electricity and used on demand to produce it.
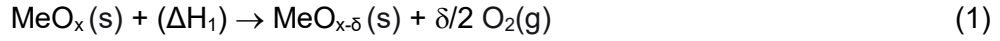
This inherent dispatchability of CSP plants without the burden of CO_2 emissions, is their "competitive edge" vs. other RE-electricity production technologies and has been identified as a key driver for the ongoing development of CSP technology despite the rapidly reducing costs of solar PVs for un-stored energy [1]. Thus, a thermal energy storage (TES) system to provide heat when sun is unavailable but high demand for electricity remains, is a necessary prerequisite condition for further commercial exploitation of CSP.

Sensible heat is the preferred heat storage type for central receiver CSP plants using air as heat transfer medium. For example, during on-sun operation of the largest such plant worldwide, Solar Tower Jülich (STJ), Germany (Figure 1a), air at atmospheric pressure is solar-heated up to about 700ºC and then powers a steam generator. In parallel, a stream of the same hot air is diverted into a sensible heat storage system integrated between the receiver and the steam turbine power generator, wherein it transfers its enthalpy to a solid medium ("charging") consisting of flow-through porous honeycombs, as it flows through it. During off-sun operation ("discharging") the air flow is reversed: "cold" air is introduced through the lower end of the already "hot" storage medium to be heated by that as it flows towards its top end, before being introduced again to the steam/power block [2]. The storage system is similar to commercial high temperature regenerative storage systems, so-called Cowper stoves used with blast furnaces, that consist of a firebrick storage medium, "charged" with hot combustion gases flowing through it and "discharged" by blowing cold air through the charged brickwork; the heated airstream is coupled back to the combustion-driven industrial processes [3].

In parallel, the majority of energy requirements of several high-temperature industries such as steel/metals, ceramics/glass, cement and chemicals, is in the form of heat (~ 70 %) [4]. Hence, in conjunction to the constantly increasing availability of "cheap" excessive power from RE sources (PV, wind, CSP) produced during daytime that cannot be introduced in the grid and has therefore to be curtailed, a recently explored approach is to convert this excess electricity into heat ("power-to-heat") and on-site supply it to such industries, decarbonizing their operation. This so-produced heat can be stored at high temperatures in an inexpensive solid heat storage material e.g. a bed of rock pebbles [5] or the Cowper regenerative heat storage systems mentioned above. In fact, industrial suppliers of such heat recovery systems, promote them as "green heat" modules [6]. Such modules essentially convert RE-electricity into heat by using an electric heater to heat air, which is then blown against the heat storage material ("bricks", rocks) to heat it ("charging"); the module is then "discharged" by blowing cold air through it, producing a heated air stream that is coupled back to the industrial processes when RE-electricity is not available. Ideas of direct resistive heating of such sensible storage brickworks with SiC heating elements powered by RE-electricity have been recently coined [3].

2. The novel concept of hybrid sensible-thermochemical storage materialized with perovskites shaped into monolithic porous structures

In previous works within joint efforts with other research groups we have demonstrated that such a CSP plant regenerative heat storage system made of flow-through porous ceramic structures can be coated with redox oxides capable of cyclic, reversible reduction/oxidation upon heating/cooling operating via redox schemes as per reactions (1)-(2), accompanied by significant heat effects. This approach hybridizes sensible with Thermochemical Energy Storage (TCS) achieving thus much higher energy storage densities in the same volume (Figure 1a). Employing Co_3O_4/CoO as redox pair oxide and evolving from small- to larger-scale porous redox structures [7], [8], [9], [10], the concept culminated in a 74 kWh$_{th}$ pilot-scale TCS unit of 90 kg of Co_3O_4 coated on cordierite honeycombs, which clearly showed reversible temperature effects on an air stream due to chemical reactions during both charging and discharging [11]; to the best of our knowledge, this unit represents the largest oxide-based TCS system developed and experimentally validated so far.

$$MeO_x (s) + (\Delta H_1) \rightarrow MeO_{x-\delta} (s) + \delta/2 \ O_2(g) \qquad (1)$$

$$MeO_{x-\delta} (s) + \delta/2 \ O_2(g) \ (+ N_2 \ (g)) \rightarrow MeO_x (s) \ (+ N_2 \ (g)) + (\Delta H) \qquad (2)$$

It is evident that the same sensible-TCS storage hybridization approach can be adopted for renewable electrification of industrial processes as well; reduction of the oxide as described above can be implemented by an air stream heated by excess RE-electricity (possibly in combination with the hot furnace exhaust gases) resulting in 24/7 supply of high-temperature heat from RE sources. Alternatively, such hybrid sensible-TCS storage systems can be coupled to power cycles to provide RE-electricity when RE sources are not available ("power-to-heat-to-power") in exact analogy with the 24/7 operation of a CSP plant. The operation principle of these concepts is schematically depicted in Figure 1b and the common overall approach summarized in Figure 1c.
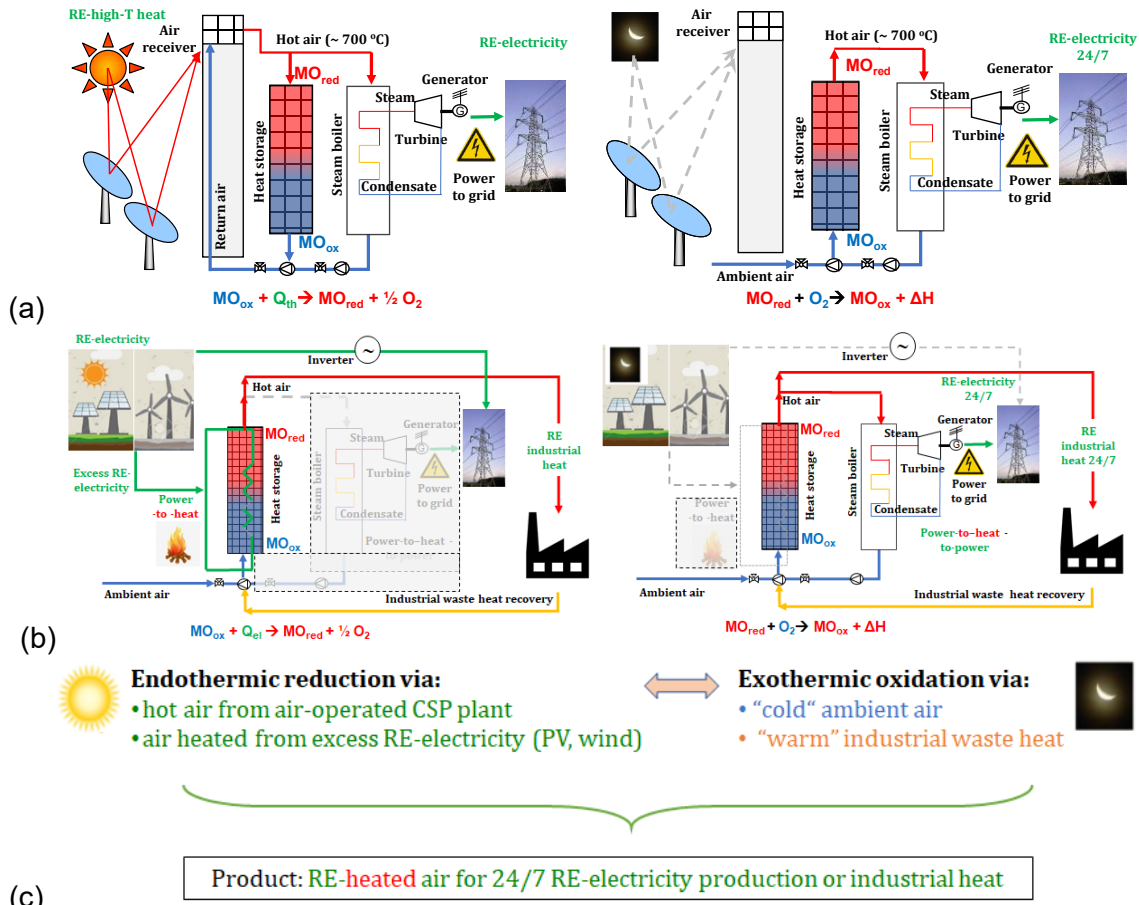
Figure 1. *The concept of hybridizing sensible with thermochemical storage in porous structured ceramics made to the highest possible degree of redox oxide pairs. (a) On- (left) and off-sun (right) operating concept schematic of an air-operated CSP plant for 24/7 RE-electricity production; (b) On- (left) and off-RE power availability (right) operating concept schematic for RE-electrification ("power-to-heat") and waste heat recovery of industrial processes, or RE-electricity production when RE sources are not available ("power-to-heat-to-power"); (parts marked in light gray do not operate during the specific step). (c) summary of the specific approach commonalities.*

It is also obvious that fabrication of the entire building blocks of ceramic monolithic structures from the redox material can maximize volumetric enthalpy yield. The challenge for such monolithic bodies is to maintain structural integrity and strength tolerating cyclic expansion/contraction due to the redox reactions without permanent dimensional changes. Despite the attractiveness of the Co_3O_4/CoO pair due to its reversible, stoichiometric redox operation and very high energy density, cobalt is expensive (~20$/kg) "critical" and potentially health-harmful. Furthermore, objects made entirely of Co_3O_4 exhibited very high permanent

"expansion" upon reduction, progressively accumulated after each cycle [12]. Thus, our research has been shifted to alternative compositions based on abundant, low-cost, non-hazardous raw materials and specifically on perovskite $CaMnO_3$–based families. These material families, suitably doped with other cations on their A- or B-site, are characterized by a combination of relevantly high specific heat - 0.82-1.0 $kJ·kg^{-1}·K^{-1}$ depending on the dopants - that is increasing with increasing temperature [13], [14], [15] and satisfactory reduction/oxidation enthalpies in the range 240 [16] - 272 [17] $kJ·kg^{-1}$ (with the reduction taking place under very low oxygen partial pressures), resulting thus high values of overall "hybrid" sensible-TCS storage in the temperature range of interest.

Dilatometry experiments with $CaMnO_3$ sintered bar specimens showed fully reversible expansion/contraction during five cycles of reduction/oxidation under air between 300-1100°C; i.e. the specimens recovered exactly their original pristine dimensions upon cooling [12]. Subsequent studies demonstrated that suitable doping of the $CaMnO_3$ composition with other cations like Sr, can extend this reversible thermochemical expansion/contraction also under very low oxygen partial pressures [18]. This unique feature renders such $CaMnO_3$-based doped perovskite compositions very attractive for the manufacture of porous structured objects, targeted on applications relevant to repetitive long-term redox cycling.

Such oxide ceramic monolithic flow-through structures can be either extruded honeycombs (like industrially practiced for the catalytic exhaust gas aftertreatment industry), or reticulated porous ceramics (RPCs also known as "ceramic foams"). These highly porous ceramic structures possess inherent advantages vs. packed powder beds, such as thin walls, high geometric surface area, good gas-solid contact and accommodation of high gas flow rates combined with low pressure drop [19]. Both these shapes are currently explored from our group within joint international projects with other research groups. The present work reports progress in the preparation and shaping of $CaMnO_3$-based from perovskite compositions and their preliminary testing with respect to cyclic reduction-oxidation.

3. Experimental

3.1 Synthesis of perovskite powders

With the strategic goal being to develop a standardized, reliable and scalable process for the synthesis of multi-cation perovskite powders in quantities necessary for the preparation of slurries and the eventual manufacture of foams, the solid-state synthesis approach was selected using as inexpensive raw materials $CaCO_3$, $SrCO_3$ (Merck, Darmstadt, Germany) and Mn_3O_4 (ERACHEM, Saint-Ghislain, Belgium) all of purity higher than 98.0 %. Precursors amounts corresponding to the targeted stoichiometry were mixed in isopropanol (solids/liquid: 1:2 wt.) under stirring for 2 hours. The solids were filtered and dried for 24h at room temperature and 24h at 80 °C and the dried powder mixture was then fired in alumina crucibles in a Carbolite RHF 14/35 muffle furnace for 24h at 1200 °C and heating/cooling rates of 5 °C min^{-1}. After this step, the product was severely sintered and therefore was dry-milled in a planetary ball mill (Fritsch Pulverisette 6) with zirconia spheres as the grinding media under conditions to ensure a final particle size distribution with 90 % of particles having diameter lower than 10 μm and a mean particle diameter of 5 μm (measured with a Malvern Mastersizer 2000® Low Angle Laser Light Scattering Analyzer), suitable for the preparation of stable, non-settling slurries. To ensure single-phase perovskite powder composition before proceeding to the preparation of slurries, XRD analysis of the calcined perovskite powder was performed (D8-Advance, Bruker diffractometer, Co-X-ray tube, Lynxe-EyeXET-Detector) in a θ-2θ-scan of the diffraction angle (2θ) 10-100° with a step size of 0.02° and 2 seconds per step.

3.2 Shaping of perovskite ceramic foams

The foam production process started with the formulation of a slurry in which 60 wt% of $Ca_{0.9}Sr_{0.1}MnO_3$ was thoroughly mixed with 34 wt% deionized water and 0.69 wt% dispersant (DOLAPIX CE64, Zschimmer & Schwarz GmbH & Co, Lahnstein Germany) with a magnetic stirrer for one hour to ensure optimum homogenization. The mixture was then gently heated to 60 °C and at this temperature 6.6 wt% (corresponding to a proportion of the total weight) binder (polyvinylpyrrolidone (PVP) K30) was added. The mixture was stirred for an additional 15 minutes to promote homogeneity. The slurry was then allowed to cool gradually to room temperature and a few drops of Kontraspum KWE antifoam agent (also from Zschimmer & Schwarz GmbH & Co, Lahnstein, Germany), were added to prevent excessive foam formation. Polyurethane (PU) foams (from HSE-FoamTec GmbH, Lüneburg, Germany) of densities in the range 20-60 ppi (pores per linear inch) were then impregnated by dipping them into the slurry. After extraction, the excess slurry is removed by applying compression to create a "green body." This resulting body is then dried overnight, followed by de-binding and sintering. Sintering was performed under air in a single-step process in which the temperature was raised to 1350 °C and maintained for 2 hours and then cooling to room temperature. The heating and cooling rates were 1°C and 2 °C min^{-1} respectively.

The porosity and pore size distribution of foam specimens were measured via mercury porosimetry (Porotec Pascal 140-440® Hg porosimeter, ThermoFisher Scientific™, Haan, Germany). Microstructural observations of the specimens by Scanning Electron Microscopy (SEM) were performed with a ZEISS ULTRA 55 FEG (Karl Zeiss, Oberkochen, Germany) instrument coupled with an INCA Pentafet x3 EDS X-ray microanalysis system from Oxford Instruments. The cyclic redox behavior of the $CaMnO_3$ foam specimens was examined by ThermoGravimetric Analysis (TGA) performed under air flow using a Netzsch STA 449 F3 Jupiter® instrument. The specimens were cycled between an upper and a lower temperature limit of 1100-300 °C respectively, with 5 °C min^{-1} heating/cooling rate. Buoyancy corrections were carried out through blank measurements.

4. Results-Discussion

After the sintering step, sturdy and rigid $Ca_{0.90}Sr_{0.10}MnO_3$ foams could be produced in a variety of diameters; from very small of the order of 10 mm targeted to be fit on the TGA holder, up to ~65 mm so far. Typical such foams are shown in Figure 2a. The largest, Ø 65 mm ones, are compared to the size of the PU templates used for the preparation in Figure 2b, so that the level of shrinkage can be appreciated. A characteristic SEM photograph of an as-manufactured foam is shown in Figure 3a. It can be seen that the foam struts have a "hollow triangular" structure, typical for ceramic foams manufactured via the polyurethane (PU) replica route [20]. The cumulative and differential pore volume distribution results of Hg porosimetry shown in Figure 3b, indicate that the foam's solid body (struts) has a porosity of 17.6 % and a mean pore diameter of ~ 48.4 μm.


| (a) | (b) | (c) |

Figure 2. (a) In-house manufactured 30 ppi $Ca_{0.90}Sr_{0.10}MnO_3$ foams of Ø 65, Ø 20 and Ø 10 mm. (b) Comparison of Ø 65 mm sintered $Ca_{0.90}Sr_{0.10}MnO_3$ foam (on top) to the Ø 80 mm PU foam template used for its preparation, to delineate shrinkage due to sintering. (c) $CaMnO_3$ foams of Ø 20 mm of 20, 30 and 60 ppi.

From the $Ca_{0.90}Sr_{0.10}MnO_3$ perovskite foams shown in Figure 2, some of the smallest size were tested in a TGA. Figure 4 shows the weight loss/gain curve of such a small foam for 32 cycles between 300-1100°C and pictures of the foam in the beginning (left) and at the end of the experiment (right). The experiment is currently ongoing in segments of 8 cycles each, targeted to reach 500 cycles. Clearly, so far, the foam has reproducible performance from cycle to cycle under no visible deformation or cracking.
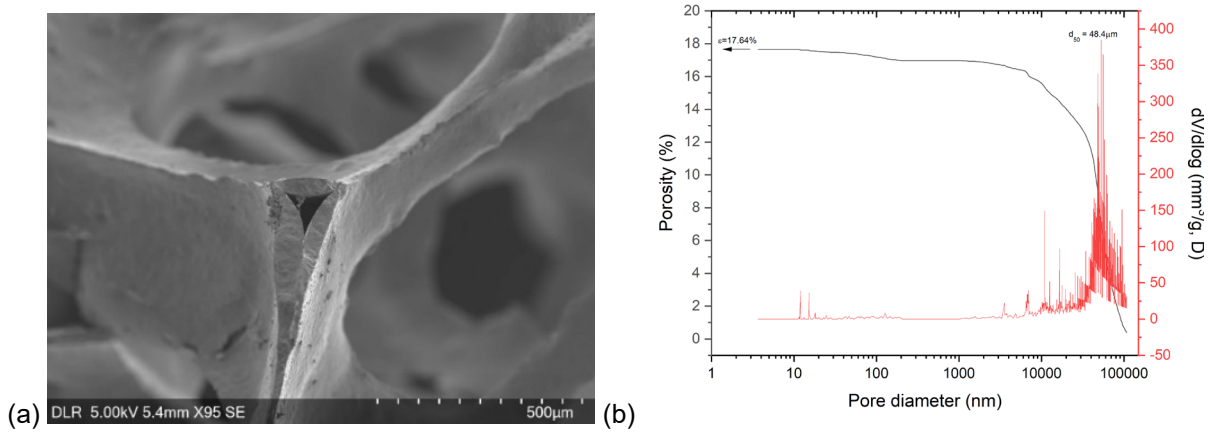
Figure 3. (a) SEM photograph of foam microstructure, indicating the hollow nature of the struts. (b) characteristic Hg porosimetry curves of such a foam (cumulative and differential) indicating (solid phase) porosity, pore size distribution and mean pore diameter
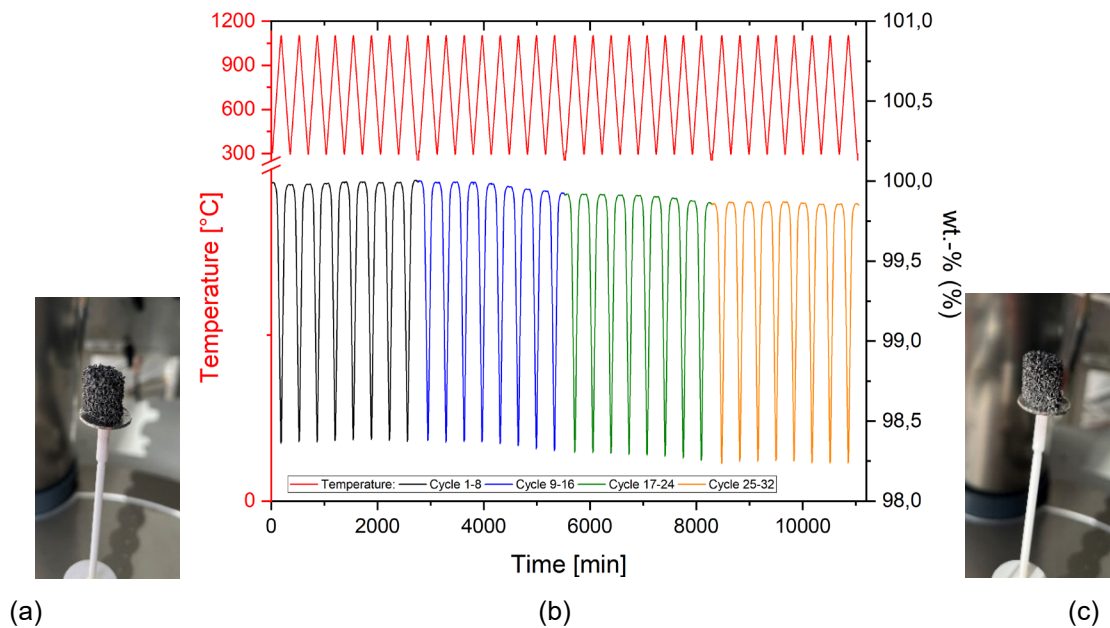
Figure 4. (a) Picture of $Ca_{0.90}Sr_{0.10}MnO_3$ foam before (b) TGA cycling of for 32 cycles between 300-1100°C; (c) picture of foam at the end of the experiment.

These attributes together with the fact that the reduction onset temperature of this perovskite upon heating under air is only around 760 °C, not only show the feasibility of the proposed concept but can open a much broader perspective for the introduction of such all-perovskite-made monolithic porous structures like honeycombs or RPCs in a variety of cyclic thermochemical processes, either directly coupled to concentrated solar irradiation or in other areas of high-temperature chemical industry. Particular advantages are evident in pressurized oxidation operation for the realization of high-efficiency Brayton power cycles in air-operated CSP plants [21], due to the well-known advantageous low pressure drop characteristics of RPCs relevant to other solid configurations like e.g. particle packed beds [22].

5. Conclusions and outlook

Our prior research efforts have demonstrated the feasibility of manufacturing porous monolithic $CaMnO_3$ perovskite structures that exhibit structural integrity and completely reversible thermochemical expansion/contraction and thus dimensional stability during thermal cycling up to 1100°C. Furthermore, this thermochemical expansion reversibility was extended at low oxygen partial pressures by proper fine-tuning of their composition with Sr. Capitalizing on these findings we have developed a standardized, scalable procedure for the manufacture of sturdy $Ca_{0.90}Sr_{0.10}MnO_3$ foams of diameters in the range 10-65 mm. Foams of the smaller size range are currently under long-term cyclic thermochemical testing and up until now have shown fully reversible redox performance without permanent dimensional changes. These features allow for direct hybridization of such structures with current state-of-the-art regenerative sensible heat storage/waste heat recovery systems of real-size CSP plants or industrial processes. Obvious benefits include higher heat storage densities in the same unit volume as well as implementation of functionalities currently not possible with conventional sensible-only storage systems.

Data availability statement

Data will be made available on request.

Author contributions

Christos Agrafiotis: Conceptualization, methodology, visualization, writing - original draft preparation, writing - review and editing, project administration, funding acquisition; Mathias Pein: Conceptualization, methodology, validation, formal analysis, investigation, resources, writing - review and editing; Asmaa Eltayeb: Conceptualization, methodology, validation, formal analysis, investigation, resources, writing - review and editing; Lena Klaas: Validation, formal analysis, investigation, writing - review and editing; Lamark deOliveira: Investigation, validation; Abhishek K. Singh: Conceptualization, writing - review and editing, funding acquisition; Martin Roeb: Resources, supervision; Christian Sattler: Resources, supervision.

Competing interests

The authors declare that they have no competing interests.

Funding

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