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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1. Introduction

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 %). Hence, a recently explored approach to the problem of excessive power from renewable energy (RE) sources (Concentrated Solar Power (CSP), PV, wind) produced during daytime that cannot be introduced in the grid and therefore has to be curtailed, is to convert this excess electricity to heat and on-site supply it to such industries, decarbonizing their operation. This so produced heat can be stored at high temperatures (~ 1000 ºC) without any scaling and physical footprint constraints. RE-electricity-heated air can be blown through an inexpensive solid heat storage material ("charging") e.g. a bed of rock pebbles or a firebrick-pattern medium with air channels like the Cowper regenerative heat storage/recovery systems of industrial blast furnaces, which 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. Alternatively, such sensible storage brickworks can be resistively-heated via RE-electricity [1]. A similar, ceramic-honeycombs-based sensible heat storage system is used in DLR's air-operated CSP plant in Juelich, Germany. In previous works we have demonstrated that this system can be made of or coated with redox oxides capable of cyclic, reversible reduction/oxidation upon heating/cooling accompanied by significant heat effects, hybridizing thus sensible with thermochemical heat storage (TCS) and achieving much higher energy storage densities in the same volume [2]. The same approach can be adopted on industrial regenerative heat storage/recovery systems, where reduction of the oxide can be implemented by either RE-electricity as described above or by the hot furnace exhaust gases (operation principle schematic in Fig. 1a) resulting in 24/7 supply of high-temperature heat from RE sources.

2. The novel concept of TCS with perovskites shaped into monolithic porous structures

Perovskite $CaMnO_3$–based material families were shaped into reticulated porous structures (RPCs, also known as "ceramic foams"- Fig. 1b) and subjected to a variety of thermochemical and thermomechanical tests. Dilatometry experiments with sintered bar specimens of $CaMnO_3$ have shown fully reversible thermochemical expansion/contraction during five cycles of reduction/oxidation under air between 300-1100ºC in contrast to other redox oxide systems investigated for the same TCS applications [3]. 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 [4]. Fig. 2 shows the weight loss/gain curve of such a small $Ca_{0.90}Sr_{0.10}MnO_3$ perovskite foam in a Thermogravimetric Analyzer (TGA) for 32 cycles between 300-1100ºC and pictures of the foam in the beginning (left) and at the end of the experiment (right). Clearly, the foam has reproducible performance from cycle to cycle under no visible deformation or cracking. 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 [5], due to the well-known advantageous low pressure drop characteristics of RPCs relevant to other solid configurations like e.g. particle packed beds.

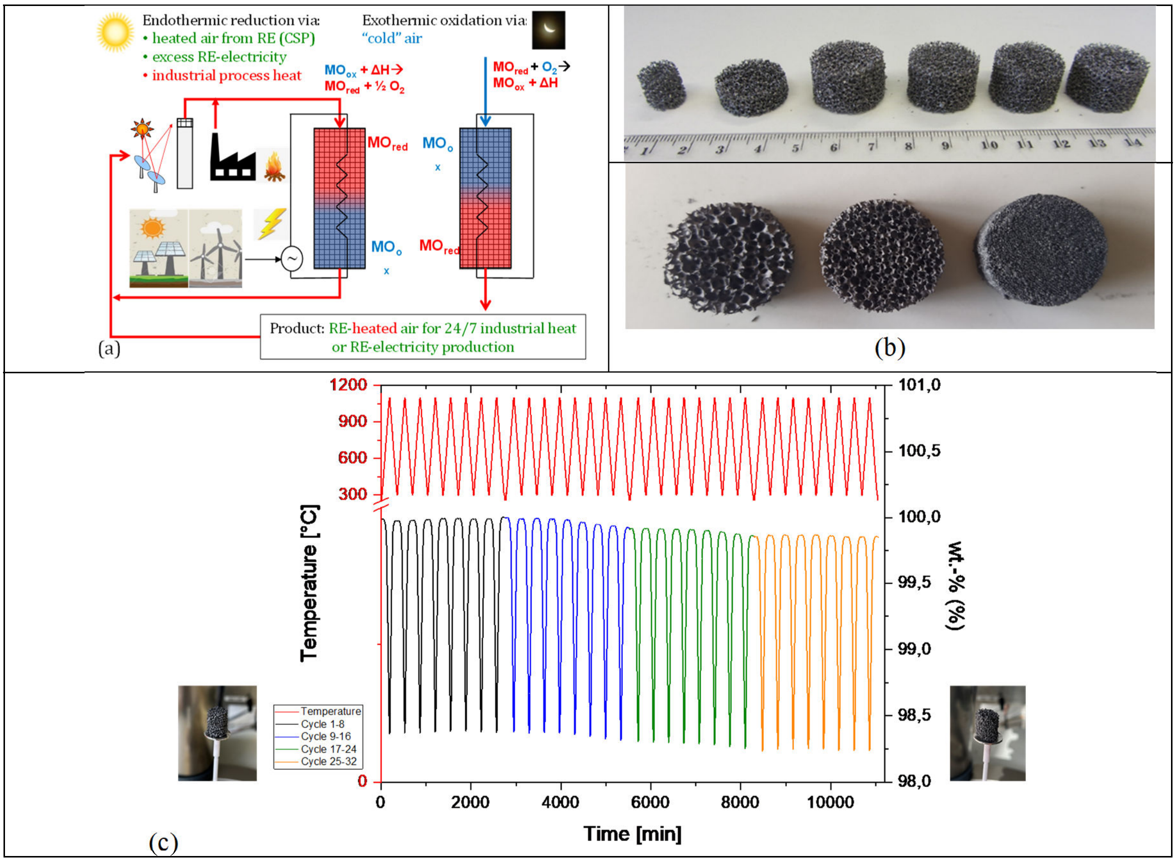

Fig. 1. (a) Schematic of overall concept implemented with non-moving hybrid sensible-thermochemical storage porous redox oxide structures reduced by various means; (b) indicative $CaMnO_3$ foams produced of various dimensions and ppi (pores per linear inch); (c) TGA cycling of $Ca_{0.90}Sr_{0.10}MnO_3$ foam for 32 cycles between 300-1100ºC and pictures of the foam in the beginning (left) and at the end of the experiment (right).

3. Conclusions and outlook

Our recent research efforts demonstrated the feasibility of manufacturing porous monolithic perovskite structures that exhibit structural integrity and completely reversible thermochemical expansion/contraction and thus dimensional stability during thermal cycling up to 1100ºC. Furthermore, this thermochemical expansion reversibility was extended at low oxygen partial pressures by proper fine-tuning of their composition. 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, such as pressurized operation for the realization of high-efficiency air-Brayton power cycles in CSP plants.

References

[1] D.C. Stack, D. Curtis, C. Forsberg, Applied Energy, 242 (2019) 782–796.

[2] S. Tescari, A. Singh, L. de Oliveira, S. Breuer C. Agrafiotis, B. Schlögl, M. Roeb, C. Sattler, Applied Energy, 189 (2017) 66–75.

[3] L. Klaas, M. Pein, P. Mechnich, A. Francke, D. Giasafaki, D. Kriechbaumer, C. Agrafiotis, M. Roeb, C. Sattler, Physical Chemistry Chemical Physics, 24 (2022) 27976-27988.

[4] M. Pein, L. Matzel, L. de Oliveira, G. Alkan, A. Francke, P. Mechnich, C. Agrafiotis, M. Roeb, C. Sattler, Advanced Energy Materials, 12(10) (2022) 2102882.

[5] A. Ambrosini, J.E. Miller, D.D. Gill, US patent US10107268 B1, (2018).