High Temperature Redox Thermochemical Heat Storage in Solar-Thermal Plants and Energy Intensive Industrial Processes

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Keywords: thermochemical heat storage, redox, perovskite, structured reactors.
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The present work relates to the presentation of a novel concept based on high temperature heat storage, with appreciable energy density, via exploitation of a hybrid sensible/cyclic reduction-oxidation (redox) thermochemical scheme that uses low cost, abundant and non-toxic ceramics bearing a perovskite structure of a general formula of ABO_3 (where A, B are metal cations and O refers to oxygen). As a representative example, the composition of $CaMnO_3$ (calcium manganite) is considered. The particular material is known to be reduced (i.e. lose oxygen) when heated up - even in air flow - in a quasi-continuous/non-stoichiometric manner and oxidized (i.e. take-up oxygen) when cooled down in O_2-containing atmosphere [Pein, 2020]. The general reaction scheme for this composition is as follows:

$$CaMnO_3 \leftrightarrow CaMnO_{3-\delta} + 0.5\cdot\delta\cdot O_2 + \Delta H_{RXN}$$

where δ is the non-stoichiometry parameter that defines the extent of the redox reaction and ΔH_{RXN} corresponds to the reaction enthalpy of the same reaction.

The concept of redox thermochemical energy storage (TCES) lies in the storage of energy, in the form of chemical bonds, during the endothermal reduction (charging) step and its release back upon triggering of the exothermal oxidation reaction (discharging). The amount of heat stored is defined by the reaction enthalpy but since such concepts also involve operation between a high and a low value of operational temperature, sensible heat storage must be also accounted for. For $CaMnO_3$ in particular, a reasonable indicative operational temperature window lies in the range of 600-1100ºC, at least when the redox scheme is destined to function under air flow. It is very important that such a redox scheme is completely reversible (i.e. no degradation with the number of redox cycles) and that the reaction enthalpy is high enough to support appreciable energy storage density. Our team has successfully validated materials and reactors, from the lab to the pilot scale and in relevant operational environment, using the cobalt/cobaltous oxide redox scheme [Karagiannakis, 2016; Tescari, 2017]. Contrary to cobalt oxide, which is expensive and potentially toxic, $CaMnO_3$ comprises only abundant and low cost elements and has already been verified to show excellent cyclability in the course of many cycles. In the frame of this work 500 redox cycles will be demonstrated to further validate this finding.
Redox TCES is particularly compatible with solar-thermal plants and especially air-operated high temperature solar power tower configurations [Alexopoulos, 2016]. It is also in-principle compatible with numerous high temperature and energy intensive processes and can substitute for fossil fuels-based generated industrial heat, provided that a source of sufficient amount and temperature thermal energy is available. This can be achieved via resistive heating powered by renewable energy sources/RES (e.g. PV or wind combined with process electrification). Indicative sketches of how such a system can be incorporated into high temperature industrial processes are provided in Figure 1.

Moreover, it is also important to define reactor designs and their associated building blocks in order to ensure maximum flexibility and adaptability to implement the envisioned TCES redox systems in as many as possible existing industrial systems. Our focus is on developing non-moving structured reactors that can ensure a number of operational advantages such as ability to allow gas flow through their mass with the minimum possible pressure drop, maximum gas-solid contact as well as elimination of complexities caused by solid particles recirculation and their storage in separate hot/cold tanks or risk of particulate matter leakages in the environment. Such candidate structured building blocks/heat storage media to construct efficient TCES reactors are shown in Figure 2 and it is important to highlight that they are all in-house manufactured.

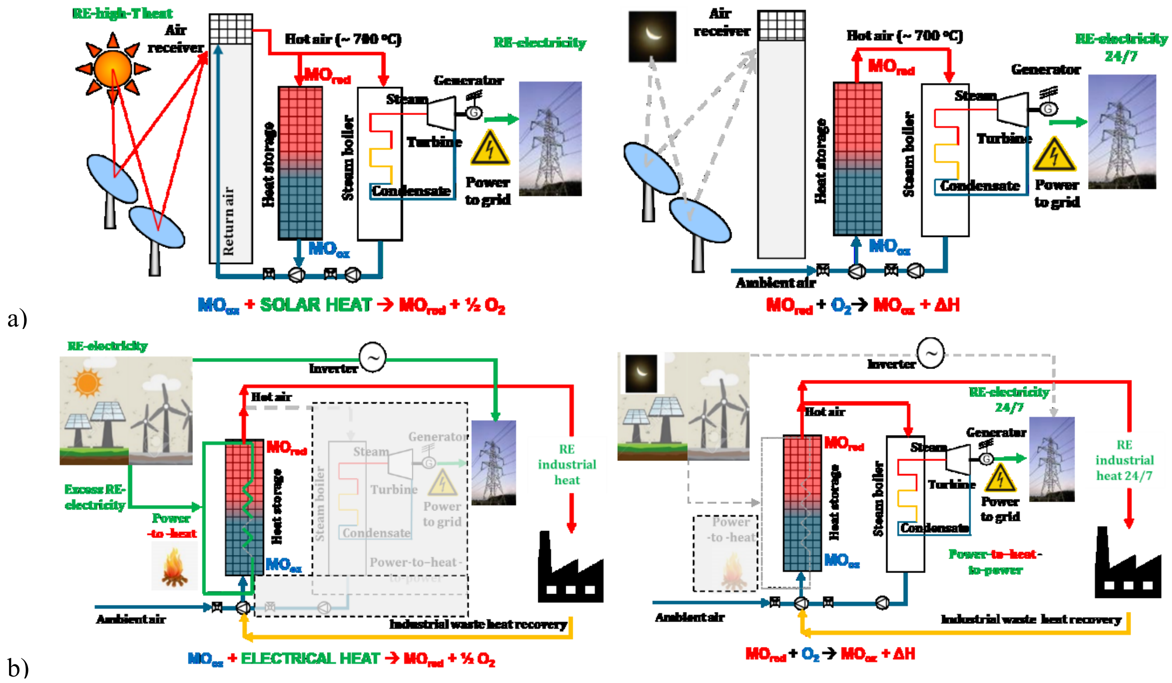

Figure 1: Indicative schematic examples showing the conceptual integration of redox TCES in a) solar thermal power tower plants and b) in industrial processes combined with process electrification and RES

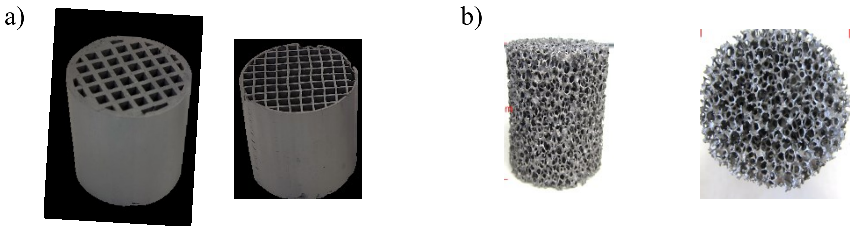

Figure 2: Examples of small-scale structured monolithic bodies entirely made from $CaMnO_3$: a) Honeycomb-like structures prepared by extrusion (two different geometries), b) foam-like structures prepared from sacrificial organic matrices

The work will also present indicative important features (i.e. energy density, information on structural stability, estimations on the redox reaction extent etc.) extracted from real experimental data, which reveal the encouraging perspectives of the associated envisioned TCES reactors and the technology as a whole. Distinct aspects of the work presented here are being developed in the framework of two EU-funded collaborative projects, with the ultimate goal being to design, construct and validate first-of-their kind experimental prototypes at the lab-to-semi-pilot scale that will clearly demonstrate the applicability of the redox TCES to a variety of high temperature processes, including solar-thermal, and their greening perspectives.

Acknowledgements
This work has received funding by the European Commission through the HORIZON EUROPE projects "*ABraytCSPfuture*" and "*HERCULES*" under grant agreement numbers 101084569 and 101104182, respectively

References
M. Pein, C. Agrafiotis, J. Vieten, D. Giasafaki, S. Brendelberger, M. Roeb, C. Sattler, Solar Energy, 198, 612-622, (2020), https://doi.org/10.1016/j.solener.2020.01.088
G. Karagiannakis, C. Pagkoura, E. Halevas, P. Baltzopoulou, A. G. Konstandopoulos, Solar Energy, 133, 394-407, (2016), https://doi.org/10.1016/j.solener.2016.04.032
S. Tescari, A. Singh, C. Agrafiotis, L. de Oliveira, S. Breuer, B. Schlögl-Knothe, M. Roeb, C. Sattler, Applied Energy, 189, 66-75, (2017), https://doi.org/10.1016/j.apenergy.2016.12.032
S. Alexopoulos, B. Hoffschmidt, WIREs Energy Environ, 6, (2017), https://doi.org/10.1002/wene.217