



# Thermodynamic potential of molten copper oxide for high temperature solar energy storage and oxygen production



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## HIGHLIGHTS

- A novel high temperature solar thermal energy storage system is presented.
- The system employs a molten metal oxide for energy storage.
- The system can achieve a high energy density of 5 GJ/m<sup>3</sup>.
- Oxygen can be also produced as a valuable by-product.

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## ABSTRACT

A novel cycle, the chemical looping of molten copper oxide, is proposed with the thermodynamic potential to achieve sensible, latent and thermochemical heat storage with an energy density of approximately 5.0 GJ/m<sup>3</sup>, which is approximately 6 times more than the 0.83 GJ/m<sup>3</sup> of molten salt. This cycle avoids the technical challenges associated with the application of solid materials (especially multivalent metals) for thermochemical energy storage such as attrition, agglomeration, particle breakage and structural change in successive reduction and oxidation reactions, although it brings alternative challenges associated with the handling of molten metal oxides. A process path for the concept is proposed based on data from the literature for the equilibrium composition of copper and oxygen at different temperatures and gas phase pressures. The process has been modelled with codes developed in MATLAB. The calculations estimate that from the total input concentrated solar thermal energy into the system, about 73% can be absorbed, while the rest is lost through re-radiation heat loss. Furthermore, it is estimated that of the absorbed heat, approximately 95% is stored, while the rest leaves the system as high temperature gas. The calculations also predict that approximately 20% of the inlet solar thermal energy is partitioned as the chemical storage, which is also employed for oxygen production. Also reported is the sensitivity to the effects of key operating parameters.

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## 1. Introduction

Among the different types of thermal energy storage (TES) systems, namely thermochemical, latent and sensible, that of thermochemical TES is of particular interest. That is because it offers the potential to achieve the greatest energy density, and hence greatest capacity to manage resource variability, together with a high storage temperature, which can contribute to an increase in the power cycle efficiency [1–3]. Of the various types of thermochemical TES such as the reduction and oxidation (Red-Ox) reactions of multivalent metal oxides [4,5], the hydration and dehydration of

alkali hydroxides [5–8] and formation and decomposition of alkali carbonates [9–12], those based on the reduction and oxidation (Red-Ox) reactions of multivalent metal oxides are of particular interest for large-scale applications. This is because these systems offer some practical advantages through the use of only air as the transported reactant since the same fluid can also act as the heat transfer fluid (HTF), avoid the need of gas storage and achieve direct heat transfer between the HTF and the storage medium [2,4]. In contrast, the hydration and dehydration of the alkali hydroxide requires the use and storage of H<sub>2</sub>O, while formation and decomposition of alkali carbonates requires the same for CO<sub>2</sub>. The latter also needs the storage of pressurised CO<sub>2</sub>, which further increases complexity of the system and costs. Multivalent metal oxides also offer the potential for high temperature storage. Thermochemical TES is potentially applicable to any high

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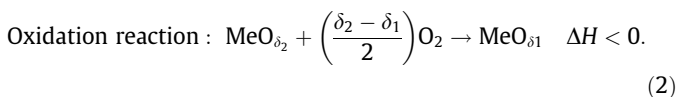
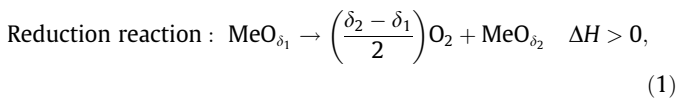
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## Nomenclature

$A_{coll}$	collector area (m <sup>2</sup> )	$\bar{\eta}_{coll}$	average collector system optical efficiency
$CR$	mean flux concentration ratio	$\sigma$	Stephan-Boltzmann constant (W/m <sup>2</sup> K <sup>-4</sup> )
$DNI$	direct normal insolation (W/m <sup>2</sup> )	$\chi_{conv,liq-sol,OxR}$	extent of conversion of Cu <sub>2</sub> O(l) to CuO(s)
$\dot{n}_{i,j}$	molar flow rate of component $i$ in stream $j$ (mol/s)	$\chi_{Q_{sol,in},O_2,prod}$	fraction of inlet solar thermal energy used for O <sub>2</sub> production
$\dot{Q}_{abs}$	absorbed power (W)	$\chi_{non,st}$	non-stored fraction of solar thermal energy
$\dot{Q}_{sol,in}$	input concentrated solar thermal power (W)	$\chi_{st}$	stored fraction of solar thermal energy
$\dot{Q}_{sol,in,max}$	maximum input concentrated solar thermal power at solar noon (W)	$\chi_{st,ch}$	chemical storage fraction
$\dot{Q}_{re-rad}$	re-radiation power loss (W)	$\chi_{st,ltnt}$	latent heat storage fraction
$T_{decom}$	decomposition temperature of CuO(s) to Cu <sub>2</sub> O(s) (K)	$\chi_{st,sen}$	sensible heat storage fraction
$T_{RR}$	reduction reactor temperature (K)		
$T_i$	temperature of stream $i$ 'th (K)		
<b>Greek letters</b>			
$\alpha_{eff}$	effective absorptance		
$\Delta H_{f,i}^0$	enthalpy of formation of component $i$ (kJ/mol)		
$\Delta H_{i,j}$	enthalpy of component $i$ in stream $j$ (kJ/mol)		
$\Delta H_{melt,i}$	enthalpy of melting of component $i$ (kJ/mol)		
$\epsilon_{eff}$	effective absorptance		
$\eta_{abs}$	absorption efficiency		
$\eta_{abs,t}$	total absorption efficiency		
$\rho_E$	energy density		
<b>Subscripts</b>			
$abs$	absorption		
$coll$	collector		
$in$	input		
$out$	output		
$melt$	melting		
$min$	minimum		
$s$	solid		
$l$	liquid		

temperature cycle, but has most commonly been assessed with concentrated solar thermal (CST) systems, since this is the leading form of high temperature heat that can be derived from an intermittent renewable resource. Those solar TES systems based on Red-Ox reactions of metal oxides comprises two steps. Firstly, the metal oxide is reduced by use of concentrated solar heat (most commonly transported as hot air) to its lower oxidation states through an endothermic reaction. Secondly, the stored heat is released during periods of low insolation through the reversible oxidation of the reduced metal oxide with air in an exothermic reaction, typically at a lower temperature. The process is then repeated [13]. However, high temperature storage, including thermochemical storage based on multivalent metal oxides is one of the least developed components of solar power plants [14]. Therefore, it is desirable to seek alternative storage cycles for efficient solar thermal energy storage that can offer improvements over currently available systems.

Oxides of multivalent metals such as Ba, Co, Cu and Mn are potential substances for high temperature thermochemical storage. These Red-Ox reactions can be described as follows [2]:



Here  $\text{MeO}_{\delta_1}$  and  $\text{MeO}_{\delta_2}$  are two states of oxidation of the metal Me. This process is sometimes also referred to as a chemical looping process, in which the state of oxidation of the metal oxide ( $\text{MeO}_{\delta}$ ) can be changed by either the temperature of the system or by the pressure of oxygen in the gas phase. For example, the equilibrium temperature for the pair of CuO(s) and Cu<sub>2</sub>O(s) is ~1030 °C at an oxygen pressure of 0.21 bar [15]. Therefore, operating at temperatures greater than 1030 °C and an oxygen pressure of 0.21 bar leads to the endothermic reduction of CuO(s) to Cu<sub>2</sub>O(s), while operation at lower temperature results in the exothermic oxidation of Cu<sub>2</sub>O(s)

to CuO(s). However, the application of a temperature swing in these types of reactions results in a decrease in the isentropic efficiency of the thermochemical TES system, due to the exergy destruction caused by the discharge temperature being lower than the charging temperature. Recently a thermochemical TES system has been proposed by Haseli et al. [16], in which the change in the pressure of oxygen in the gas phase is proposed as the driving force of the Red-Ox reactions employed for thermochemical TES. In this system steam is proposed to be injected as an inert gas (in the considered operating conditions) into the solar reduction reactor, where CuO (s) is reduced endothermically, to lower both the reduction temperature and the storage temperature because of the lower partial pressure of oxygen. At the same time the oxidation reactor is proposed to be pressurised to increase the temperature of the oxidation reaction and hence the release temperature of the stored energy. Advantageously, this concept is shown to lower the gap between the oxidation and reduction temperatures, which in turn increases the exergy efficiency of the system. It also offers potential to produce industrially pure oxygen, which boosts the economic viability of the system.

The application of the solid metal oxides in thermochemical storage systems, regardless of the process configuration, limits the charge/discharge temperatures to typically around 1000 °C [17], to avoid softening, sintering or other damage to the solid storage medium. This is significantly lower than the state-of-the-art in commercially available gas turbines, which is currently around 1250 °C [18–20], thereby lowering the maximum thermodynamic efficiency of the solar thermal combined cycle power plants with this type of storage. Furthermore, the life of the solid metal oxides used as the chemical storage medium, is limited by the chemical/physical damages due to thermal shock, agglomeration, erosion, abrasion and changes in crystalline structure that occurs in consecutive Red-Ox reactions.

One possible approach to address the aforementioned limitations of the solid thermochemical storage mediums is to use a liquid metal oxide as the medium throughout the processes of oxidation, reduction and storage. This approach has potential to avoid the limitations associated with the use of solid particles to enable operation at higher temperatures. It also offers the potential

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