

# Thermodynamic and kinetic investigation of a technical grade manganese-iron binary oxide for thermochemical energy storage



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## ARTICLE INFO

### Article history:

Received 27 January 2017

Received in revised form 1 May 2017

Accepted 12 May 2017

### Keywords:

Thermochemical energy storage

Redox reaction

Manganese-iron oxide

Thermodynamic equilibrium

Thermal hysteresis

Gas-solid reaction kinetics

## ABSTRACT

Thermochemical energy storage (TCS) based on gas-solid reactions constitutes a promising concept to exploit reaction enthalpies for thermal energy storage. This concept facilitates the development of efficient storage solutions with higher energy densities compared to widely investigated sensible and latent thermal energy storage systems. Multivalent metal oxides are capable of undergoing a reversible redox reaction at high temperatures, which is why those storage materials are considered particularly suitable for the operating temperature range of concentrated solar power plants with central receiver systems to increase the total plant efficiency and ensure dispatchability of electricity.

In the scope of this work a granular manganese-iron oxide with a Fe/Mn molar ratio of 1:3 has been selected as a potentially suitable storage material, which is non-toxic, abundant and economical. For this reason a preparation route from technical grade raw materials has been chosen. The reversible redox reaction is investigated with respect to the thermodynamic and kinetic characteristics by means of simultaneous thermal analysis in dynamic and isothermal series of measurements. Those revealed that the observed presence of a strong divergence of the reactive temperature range from the actual thermodynamic equilibrium can mainly be attributed to kinetic limitations. Expressions for the effective reaction rates are deduced from experimental data for the reduction and oxidation step, describing the dependence of the reaction rate on temperature and oxygen partial pressure, respectively. The expressions are valid for the temperature ranges in proximity to the equilibrium, which are relevant for the targeted operating conditions of the storage reactor in air. The storage material provides good cycling stability in terms of reversibility and widely maintained reactivity throughout 100 redox cycles in air. Future work comprises material modifications, which are expected to further enhance the mechanical stability of the particles. Overall, the manganese-iron oxide of the chosen composition exhibits a redox reactivity practical for regenerator-type storage systems combining a high temperature TCS zone and a lower temperature non-reactive zone merely used for sensible thermal energy storage.

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## 1. Introduction

The development of sustainable energy systems based on renewable energy sources is important to decrease the dependence on fossil fuels and reduce CO<sub>2</sub> emissions. Concentrated solar power (CSP) plants constitute a promising alternative technology for electricity generation in regions with high solar irradiation (Pfenninger et al., 2014). The integration of a high temperature thermal energy storage (TES) system into a CSP plant is one of the most important aspects, since it increases the plant's dispatchability and efficiency

of the electricity generation. The storage of thermal energy on a large scale allows to mitigate short fluctuations in solar irradiation, bridge short-term deficiencies during cloud passage and extend electricity production into the nighttime hours (Liu et al., 2016).

In general, research on the identification and improvement of materials as well as on the design of reactor concepts for thermochemical energy storage (TCS) is still at an early stage (Pardo et al., 2014). Current investigations for high temperature storage applications from ~600 °C up to even ~1100 °C are focused on redox cycles employing multivalent metal oxides, which have the potential to undergo reversible redox reactions to store thermal energy in form of the reaction enthalpy ( $\Delta_r H$ ) according to the following pathway:

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## Nomenclature

### Abbreviations

B	cubic bixbyite phase (Mn,Fe) <sub>2</sub> O <sub>3</sub>
CLOU	chemical-looping with oxygen uncoupling
CSP	concentrated solar power
DSC	differential scanning calorimetry
g	gaseous
HTF	heat transfer fluid
N <sub>2</sub>	nitrogen
O <sub>2</sub>	oxygen
redox reaction	reduction-oxidation reaction
s	solid
S	cubic spinel phase β-(Mn,Fe) <sub>3</sub> O <sub>4</sub>
SEM	scanning electron microscopy
STA	simultaneous thermal analysis
T	tetragonal spinel phase α-(Mn,Fe) <sub>3</sub> O <sub>4</sub>
TCS	thermochemical energy storage
TES	thermal energy storage
TGA	thermogravimetric analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence

### Symbols

A	pre-exponential factor (1/s)
β	heating rate or cooling rate (K/min)
Δ <sub>R</sub> H	molar reaction enthalpy (kJ/mol)
Δ <sub>R</sub> h	specific reaction enthalpy (kJ/kg)
Δ <sub>R</sub> G	Gibbs free energy of reaction (kJ/mol)
Δ <sub>R</sub> S	molar reaction entropy (J/(mol·K))
E <sub>a</sub>	activation energy (kJ/mol)

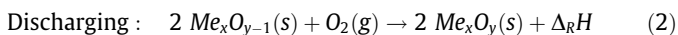
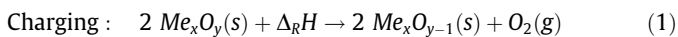
f(X)	reaction model, reaction mechanism (-)
g(X)	integral form of the reaction model (-)
h(pO <sub>2</sub> , pO <sub>2,eq</sub> )	pressure-dependent function, pressure term (-)
k(T)	rate constant (1/s)
K <sub>eq</sub>	equilibrium constant (-)
m	mass (g)
m	exponent of pressure term (-)
n	parameter of reaction model (-)
ν <sub>O<sub>2</sub></sub>	stoichiometric coefficient of oxygen (-)
p <sub>ambient</sub>	atmospheric pressure (Pa)
pO <sub>2</sub>	oxygen partial pressure (Pa)
pO <sub>2,eq</sub>	oxygen partial pressure at equilibrium (Pa)
t	time (s)
t <sub>0</sub>	delay period (s)
T	temperature (K)
X	reaction conversion (g/g)
y <sub>O<sub>2</sub></sub>	molar fraction of oxygen (-)

### Constants

R	molar gas constant (J/(mol·K))
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### Subscripts

c	charging
d	discharging
eq	equilibrium
Ox	oxidation
Red	reduction



Some metal oxides possess the intrinsic advantage to react reversibly with oxygen (O<sub>2</sub>) at high temperatures. Hence, the concept provides the possibility to utilize ambient air simultaneously as carrier of the reaction gas O<sub>2</sub> and heat transfer fluid (HTF). This approach facilitates a direct contact heat transfer between the gas (air) and the solid storage material (metal oxide). An additional high temperature heat exchanger is therefore not necessary.

The thermal charging process is achieved by means of the endothermic reduction step driven by solar thermal energy under the release of O<sub>2</sub> (1), which process can be either performed directly in the solar central receiver or indirectly in a TCS reactor using the HTF air. The reduction step is accompanied by the advantage of a facile separation of the gaseous product from the reduced solid in order to prevent re-oxidation for the period of storage. The recombination of the reduced metal oxide and O<sub>2</sub> (from ambient air) leads to the exothermic oxidation step, representing the thermal discharging process by the complete recovery of thermal energy via the release of the heat of reaction (2). This storage concept based on metal oxides offers process-technological advantages compared to the use of other TCS materials, since there is no necessity for intermediate storage of the reactant gas. Consequently, a storage reactor could potentially be implemented into a CSP plant in the form of an open-loop system. The use of air as HTF allows to work with high HTF temperatures up to and even beyond 1000 °C, which renders TCS reactors based on metal oxides specifically interesting for solar tower CSP plants with a future generation of central receiver technology (Ávila-Marín, 2011; Ho, 2017).

The high degree of thermal energy stored as sensible heat due to the elevated working temperatures – temperatures above the reduction temperature in the charging stage – can be regarded as one of the most important intrinsic aspects and also challenges of high temperature TCS based on metal oxides. On this account hybrid storage concepts using sensible and thermochemical energy storage simultaneously in one single storage unit have been suggested to enhance the overall energy storage density. In view of a packed bed storage unit, this concept would facilitate an increase in volumetric and gravimetric energy storage densities of the solid inventory due to a high temperature TCS zone as well as cost savings due to a low temperature non-reacting cooling section employing low cost inert materials as sensible storage media (Ströhle et al., 2016). As indicated in Fig. 1, the reactive material would only be positioned in the upper part of the packed bed storage, where operating conditions during charging allow the reduction to take place. The operating method is comparable to high temperature regenerator-type storage systems, so called passive dual media TES systems with gaseous heat transfer medium and solid storage medium. During the charging stage hot air from the solar field enters the storage at the top and flows downward, forming a characteristic transient temperature profile along the axis of the solid inventory (Fig. 1(a)). The direction of the flow is subsequently reversed in the discharging stage, cold air entering at the bottom of the storage (Fig. 1(b)). In this way an axial thermal stratification inside the packed bed can be maintained, when thermal energy is transferred to and extracted from the storage (Zanganeh et al., 2012; Zunft et al., 2011).

In this work, we performed the examinations with regard to the envisaged technical application of a hybrid regenerator-type storage with direct contact heat transfer between the HTF and the solid inventory in the form of a packed bed configuration. Therefore, a

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