Solar Energy 174 (2018) 617–627

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on Fe_2O_3/Fe_3O_4 redox reactions: Thermodynamic and kinetic analyses

H. Evan Bush, Peter G. Loutzenhiser*

George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0405, USA

ARTICLE INFO

Keywords:
Concentrated solar energy
Thermochemical energy storage
Iron oxide
Thermodynamic analysis
Kinetic analysis

ABSTRACT

Solar electricity production via an Air Brayton cycle is considered with integrated thermochemical energy storage. The storage is realized via a two-step solar thermochemical cycle based on Fe_2O_3/Fe_3O_4 reduction-oxidation reactions, encompassing (1) the thermal reduction of Fe_2O_3 to Fe_3O_4 and O_2 driven by concentrated solar irradiation under vacuum; and (2) the exothermic oxidation of Fe_3O_4 with a compressed air stream back to Fe_2O_3. The steps may be decoupled, resulting in a high temperature, pressurized airflow that is expanded across a turbine to produce on-demand electricity. A thermodynamic analysis of the system determined a maximum cycle efficiency of 46.0% at a solar concentration ratio of 4000 suns, an oxidation pressure of 30 bar, and an approximately 5:1 molar flow rate ratio of air to solid Fe_2O_3 exiting the re-oxidizer. Chemical kinetics for the thermal reduction of Fe_2O_3 were determined between approximately 1400 and 1700 K using non-isothermal thermogravimetry with heating rates between 10 and 20 $K{\cdot}s^{-1}$ and O_2 partial pressures between 0 and 0.05 bar. The rate-limiting reaction mechanism was determined to be nucleation, and kinetic parameters were resolved using an Avrami-Erofe'ev nucleation model with a reaction order of 1.264 ± 0.010. The rate constant followed an Arrhenius-type temperature dependency with an apparent activation energy of 487.0 ± 3.6 $kJ{\cdot}mol^{-1}$ and pre-exponential factor $2.768 \pm 0.783{\cdot}10^{14}$ s^{-1}. A power-law dependence on O_2 partial pressure of order 8.317 ± 0.233 was determined. Non-isothermal thermogravimetry to examine the oxidation of Fe_3O_4 to Fe_2O_3 revealed multiple kinetic regimes, and isothermal thermogravimetry showed the reaction proceeded rapidly, within 20 s, at temperatures greater than 673 K. Solid characterization was carried out using scanning electron microscopy and x-ray powder diffractometry up to temperatures of 1073 K to verify initial and final sample compositions and structures.

1. Introduction

In previous works, thermodynamic and kinetic analyses were used to examine electricity production in an Air Brayton cycle with integrated solar thermochemical energy storage (TCES) based on Co_3O_4/CoO oxidation-reduction (redox) reactions at a solar concentration ratio of 1000 suns (where 1 sun = 1 $kW{\cdot}m^{-2}$) (Muroyama et al., 2015; Schrader et al., 2017; Schrader et al., 2015). TCES based on the Co_3O_4/CoO redox pair is especially promising due to rapid achievable reaction rates, a high reaction enthalpy, and cyclability of the reversible oxidation/thermal reduction reactions. However, cobalt oxides are relatively sparse and expensive (Wong, 2011) and pose potential human and environmental health concerns (SIGMA-ALDRICH, 2017). The Co_3O_4/CoO redox pair also thermally reduces at a lower temperature compared to other redox pairs, reducing the maximum achievable cycle efficiency and producing a mismatch in pairing to solar concentrating infrastructure capable of achieving higher solar concentration ratios (Steinfeld and Palumbo, 2001).

The purpose of this work is to thermodynamically and kinetically examine a similar cycle based on the Fe_2O_3/Fe_3O_4 redox pair. Fe_2O_3/Fe_3O_4 is one of many metal oxide candidates proposed for TCES applications, including the Co_3O_4/CoO (Agrafiotis et al., 2014; Hutchings et al., 2006; Neises et al., 2012; Pagkoura et al., 2014), Mn_2O_3/Mn_3O_4 (Alonso et al., 2013; Carrillo et al., 2014), CuO/Cu_2O (Alonso et al., 2015; Deutsch et al., 2017; Haseli et al., 2017), and BaO_2/BaO (Bowrey and Jutsen, 1978; Carrillo et al., 2016) binary pairs, as well as a number of mixed ionic-electronic conducting metal oxides, which have the advantages of continuous redox equilibria, tunable thermodynamic properties, high reaction rates, and large redox capacities without departure from the perovskite phase (Babiniec et al., 2015, 2016;

---

* Corresponding author.
E-mail address: peter.loutzenhiser@me.gatech.edu (P.G. Loutzenhiser).

https://doi.org/10.1016/j.solener.2018.09.043
Received 14 July 2018; Received in revised form 14 September 2018; Accepted 16 September 2018

Nomenclature

ΔG	Gibbs property/free enthalpy
ΔH	enthalpy of reaction
Δm	TGA mass loss/gain
A	undetermined constant
C	solar concentration ratio (relative to 1 $kW{\cdot}m^{-2}$)
D	maximum particle size for oxidation of magnetite to maghemite
E_a	apparent activation energy
f	model equation/kinetic solid conversion dependence (differential form)
h	kinetic O_2 partial pressure dependence
k	rate constant/kinetic temperature dependence
k_0	apparent pre-exponential/frequency factor
m	mass, partial pressure-dependence rate constant
n	Avrami-Erofe'ev rate constant
$\dot{n}$	molar flow rate
p	pressure, unknown model parameter
$\dot{Q}$	heat transfer rate
r	reaction/temporal conversion rate
r^2	coefficient of determination
R	universal gas constant
SSE	sum of squared errors/residual sum of squares
t	time
T	temperature
$\dot{W}$	power
x	nonstoichiometry

Greek letters

α	conversion, hematite
β	TGA heating rate
γ	maghemite
η	efficiency

Subscripts

∞	equilibrium value
0	environment/dead state (298.15 K and 1 bar), initial value
air	air, approximated as a 21% O_2–N_2 concentration ideal gas mixture
comp	cycle air compressor (for re-oxidizer) stage
cool	receiver outlet O_2 cooling/quench stage
cycle	combined thermochemical and Air Brayton cycle
eq	thermodynamic equilibrium
exhaust	air stream exiting turbine
g	gas state
i	index variable
j	index variable
loss	re-radiative and convective thermal losses
m	maximum
oct	octahedrally-configured
reactor	cycle solar receiver/reactor (reduction) stage
recover	Fe_2O_3/Fe_3O_4 particle stream exiting re-oxidizer
solar	cycle solar thermochemical reactor stage
tet	tetrahedrally-configured
turbine	Air Brayton cycle turbine stage
vac	cycle vacuum pump (for solar receiver/reactor) stage

Superscripts/accents

ˆ	dependent variable, model estimate

Acronyms

AN	nth-order Avrami-Erofe'ev nucleation-limited model
FCC	face-centered cubic or cubic close-packed crystalline structure
HCP	hexagonal close-packed crystalline structure
SEM	scanning electron microscopy
TCES	thermochemical energy storage
TGA	thermogravimetric analysis/analyzer
XRD	X-ray diffractometry

Imponenti et al., 2017; Zhang et al., 2016). Fe_2O_3/Fe_3O_4 redox reactions are particularly attractive because Fe_2O_3 has a higher thermal reduction temperature than most other binary candidates, permitting higher theoretical Air Brayton cycle efficiencies. The Fe_2O_3/Fe_3O_4 redox pair materials are also are relatively inexpensive and widely available compared to Co_3O_4/CoO materials, and they carry fewer environmental/human health concerns (Smith and Huyck, 1999), making the redox pair a more practical and economically appealing candidate for large-scale deployment. The reversible redox reaction of Fe_2O_3/Fe_3O_4 is represented as:

$$3Fe_2O_3 \leftrightarrow 2Fe_3O_4 + \frac{1}{2}O_{2(g)}\,, \quad \Delta H_{298.15\,K} = 78.3\,kJ{\cdot}mol^{-1} \tag{1}$$

Iron oxides have been the focus of numerous solar thermochemical studies, including carbothermal iron production (Steinfeld and Fletcher, 1991), fuels co-production via carbothermal reduction and/or methane cracking (Halmann and Steinfeld, 2006; Steinfeld et al., 1995; Steinfeld et al., 1993; Tamaura et al., 1997), and H_2O and/or CO_2 splitting via two-step cycles based on Fe_3O_4/FeO redox reactions (Galvez et al., 2008; Loutzenhiser et al., 2009; Nakamura, 1977; Sibieude et al., 1982; Stamatiou et al., 2010). For the Fe_2O_3/Fe_3O_4 pair, the high Fe_2O_3 thermal reduction temperatures have presented both materials compatibility and engineering design challenges. Such concerns have prompted the study of combined oxides of iron and other multivalent metals, with the goal of lowering the thermal reduction temperature (André et al., 2017; Block et al., 2014; Block and Schmücker, 2016; Pagkoura et al., 2014). However, past efforts have shown a significant decrease in reaction enthalpy.

In this study, the Fe_2O_3 thermal reduction temperature was reduced by operating at decreased O_2 partial pressures to shift the equilibrium to a more favorable temperature range according to Le Chatelier's principle. The impact of decreasing the O_2 partial pressure is shown in Fig. 1. For an O_2 partial pressure of 10^{-3} bar, Fe_2O_3 begins to reduce to Fe_3O_4 at a temperature of 1432 K. The Fe_2O_3/Fe_3O_4 pair allows for higher oxidation temperatures and, therefore, greater Air Brayton cycle theoretical efficiencies, at the cost of decreasing receiver absorption efficiencies due to greater re-radiative losses to the environment (Steinfeld and Palumbo, 2001). Therefore, a comprehensive thermodynamic cycle analysis was performed to assess the potential of the Fe_2O_3/Fe_3O_4 pair.

An analysis of Fe_2O_3/Fe_3O_4 TCES integrated into an Air Brayton cycle was performed as a function of molar flow rate of air, reactor temperature, compressor outlet/turbine inlet pressure, and solar concentration ratio. The thermal reduction and oxidation reactions were examined using thermogravimetric analysis for a range of heating rates and O_2 partial pressures to measure reaction rates, identify rate limiting mechanism(s), and determine kinetic parameters. A cycling study was performed to examine material stability and scanning electron