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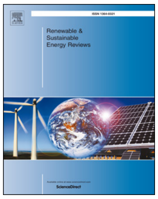

A review of material screening in pure and mixed-metal oxide thermochemical energy storage (TCES) systems for concentrated solar power (CSP) applications

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ABSTRACT

Thermochemical energy storage (TCES) systems have attracted great interest in concentrated solar power (CSP) applications during past years. Storing sunlight as chemical energy during the day enables us to use it at night or during cloudy periods, which alleviates the inherent intermittency of solar sourced energy. Metal oxides are among the most attractive TCES materials, as they possess high-energy density and high reduction/oxidation temperatures which are suitable for driving high-efficiency thermodynamic power cycles. Although various candidate materials have already been introduced in metal/mixed-metal oxide TCES technologies, material selection is still a challenging process, since it has a profound impact on overall cost and performance of TCES technologies. This article focuses on a comprehensive literature survey on material screening in metal/mixed-metal oxide TCES systems introducing pros and cons of each candidate material. Although the screening indicated high potential candidate materials for TCES technologies, further investigations are required in this field to develop TCES systems which are compatible with CSP applications.

1. Introduction

The present global energy model is mainly based on the use of fossil fuels which has implications for national security, the environment, and the economy [1]. Renewable energy sources are attractive alternatives to replace fossil fuels because of their promising social, environmental, and economic benefits [2]. The International Energy Agency (IEA) predicted that the share of renewable energy in the energy market will increase from around 13.2% of its total primary energy supply in 2012 to 26% in 2020 [1].

Solar energy is one of the most abundant and cleanest types of renewable energy sources. Concentrating solar power technologies (CSP) convert sunlight into thermal power which traditionally used as a heat source for power generation by thermodynamic cycles. CSP technologies can also be used to drive endothermic chemical processes such as fuel production, material processing, and chemical commodity production [3]. Although CSP can provide clean energy to meet the world's annual demand, its intermittence presents a technical challenge [4]. Thermal energy storage (TES) systems can be used to match solar transience to electrical demand to overcome solar intermittency [4]. In general, TES systems can be divided into three main types; sensible heat storage (SHS), latent heat storage (LHS), and thermochemical energy storage (TCES) [5–10].

1.1. *Thermal energy storage systems (TES)*

Intermittency is the main issue of using solar energy [4]. Using a backup system which stores energy in on-sun hours to use it in off-sun time is the solution for the mentioned challenge [5]. In the backup system, we need to use fossil fuel or bioenergy such as biomass as a source of energy system which has its own pollution problem. Therefore, one of the clean and sustainable solutions for the intermittency issue of solar energy is using TES systems. As mentioned earlier, TES technologies can be divided into three distinct groups which are SHS, LHS, and TCES systems [5–11].

1.1.1. *Sensible heat storage (SHS)*

SHS systems use liquid or solid media in order to store and release energy without any phase change [10]. In general, SHS systems are being used in lower temperatures compared to LHS and TCES, SHS technologies, but SHS systems are commercial, simple, easy to control, and cheap [6,8,10,12]. However, SHS systems have low energy density

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compared to LHS and TCES systems [13]. A comprehensive study has been done by Khare et al. [10] in order to select materials for SHS system in high temperatures ($> 500\,^{\circ}C$). They reported that some common materials such as high temperature concretes, alumina, silicon carbide, cast iron, graphite, and steel are potential candidate materials for SHS in the range of 500–750 °C. Among these materials, high temperature concretes have the lowest price in SHS technologies [10]. The current focus of researchers in the field of SHS systems is on developing new heat transfer fluids (HTF) such as molten salts which are compatible with high temperature CSP technologies [10,14–16]. Molten salts have some advantages such as appropriate thermal stability and lower melting points (around 200 °C) which make them as an appropriate HTF for CSP technologies. However, molten salts are suffering from high corrosion [14]. Liu at al. [17] and Vignarooban et al. [14] summarized new development in molten salt systems and new HTFs.

1.1.2. Latent heat storage (LHS)

LHS systems are using phase change materials to store and release energy [10]. Since storing the gas is difficult, LHS technologies are usually using solid to liquid phase transition rather than liquid to gas phase change [13,18]. In general, energy density of LHS technologies is higher than SHS systems, but it is lower than the energy density of TCES technologies [13]. The main drawback of LHS systems is their low thermal conductivity which is around 0.2–0.8 W/mK [11]. LHS systems have been reviewed in literature by e.g. Gil et al. [9].

1.1.3. Thermochemical energy storage (TCES)

In general, high operating temperatures are required in energy cycles to have higher thermal efficiencies. In this respect, SHS and LHS systems have upper temperature limitations. Although these systems are state-of-the-art and also much easier to handle at low operating temperatures, corrosion effects make them more complicated at temperatures higher than 600 °C [19]. In addition, sensible heat storage systems require high quantities of storage media, which increases the overall cost [13]. TCES technologies not only work in high temperatures, but also they have high energy density [8,20]. Pardo et al. [12] reported that for selected TCES systems, volumetric energy density is about five to ten times higher than the studied LHS and SHS candidate materials. In addition, chemical products can be stored in ambient temperature, which reduces thermal losses in these systems [21]. Therefore, in high temperature storage systems, TCES systems are promising technologies.

TCES systems are based on reversible chemical reactions in which energy is stored in the form of chemical bonds as follows:

$$A + heat\,(\Delta H_{chemical\ reaction}) \leftrightarrow B + C. \tag{1}$$

In forward step of reaction (1), component A decomposes into components B and C which is called charging, and it is an endothermic process [22]. In CSP technologies, charging reaction happens during the day when sun is available as a source of energy. At night or in cloudy period, backward reaction (discharging) takes place which is an exothermic reaction realising produces stored energy. Fig. 1 shows schematics of TCES systems using CSP technologies.

Fig. 2 shows the classification of TCES systems at medium and high operating temperatures, which are favorable for CSP technologies. For operating temperatures higher than 700 °C, metal/mixed-metal oxide redox cycles are much more promising. They can not only work in higher temperatures, but also they have longer storage durations at near ambient temperature [24], and higher energy storage capacity thanks to high enthalpy of the reaction [13]. Metal/mixed-metal oxide redox cycles have been used for multiple solar thermal applications for hydrogen production by water-splitting (WS) [25–30] and syngas production by carbone dioxide-splitting (CDS) [26,31] as well as TCES technologies [3,19,32]. The only difference between the TCES systems with WS and CDS systems (fuel application) is that water and carbon dioxide are used instead of oxygen in re-oxidation step to oxidize the redox materials in WS and CDS, respectively. Reactions (2)–(7) show the redox cycles for WS, CDS, and TCES technologies, respectively.

Redox reaction form for WS systems:

$$\text{Reduction step: } MO_{ox}+heat(\Delta H_{reaction})\rightarrow MO_{red}+0.5O_2. \tag{2}$$

$$\text{Re}-\text{Oxidation step: } MO_{red} + H_2O \rightarrow MO_{ox} + H_2. \tag{3}$$

Redox reaction form for CDS systems:

$$\text{Reduction step: } MO_{ox}+heat(\Delta H_{reaction})\rightarrow MO_{red}+0.5O_2. \tag{4}$$

$$\text{Re}-\text{Oxidation step: } MO_{red} + CO_2\rightarrow MO_{ox}+CO. \tag{5}$$

Redox reaction form for TCES systems:

$$\text{Reduction step: } MO_{ox}+heat(\Delta H_{reaction})\rightarrow MO_{red}+0.5O_2. \tag{6}$$

$$\text{Re}-\text{Oxidation step: } MO_{red} + O_2\rightarrow MO_{ox}. \tag{7}$$

In reactions (2)–(7), M is a metal.

It is also feasible to use other gases such as air as an oxidizer instead of pure oxygen in Eq. (7). Redox system is called open loop system when ambient air is used as the oxidizer in re-oxidation step [13,33]. One of the advantages of the open loop TCES systems is that there is no need to store HTF [13]. In addition, there is no need for high temperature heat exchanger in open loop systems, which decreases overall heat loss in TCES systems [34]. TCES systems can be divided into low temperature and high temperature systems although high-temperature TCES systems have high thermal efficiency. Both low- and high-temperature TCES systems can be used for energy storage applications. In this regard, solar thermal energy is stored in the form chemical potential during the charging process, and it is released during discharging process in order to overcome solar intermittency [35,36]. Therefore, thermos-physical properties, heat and mass transfer of materials and thermodynamic configurations influence energy density of TCES systems [37–40].

Minimum and maximum threshold operational temperature for a CSP technology is 400 and 1200 °C, respectively (thus compatible with parabolic trough or solar tower systems) [13]. In this temperature range, however, higher temperature is desirable for TCES system because of high thermal efficiency. In this regard, metal/mixed-metal oxide TCES systems are the next generation of the industrial TES technologies for CSP applications. Therefore, material screening is vital to choose a candidate material with high energy storage density and appropriate redox reaction temperature range which is compatible with the temperature range of CSP technology (400–1200 °C).

To the best of our knowledge, there is no industrial-scale metal/mixed-metal oxide TCES system which is coupled with CSP as it is a new generation in CSP technology. However, several research studies have been carried out in lab-scale reactors which are compatible with concentrated solar power systems. In this regard, one of the most interesting systems is a directly irradiated rotary kiln as it can provide high mass flow rates and also high amount of active material. Rotary kiln has already installed and tested in a lab-scale solar furnace, which is completely compatible with different types of metal and mixed metal oxide TCES systems [41–43]. A similar reactor has also been used for lime production [44–46]. A comprehensive literature review has been done by Alonso et al. [47] in the field of rotary kiln design for solar thermal applications including TCES systems coupled with CSP technologies. Alonso and Romero [48] also designed a CSP assisted fixed-bed reactor in a lab scale with is compatible with different metal oxide TCES systems. For aforementioned reactors, concentrated solar power can be provided using heliostats and mirror concentrator.

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