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Comparing the thermodynamic potential of alternative liquid metal oxides for the storage of solar thermal energy

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A B S T R A C T

The relative potential of liquid multivalent metal oxides for the storage of thermal energy as sensible, latent and/or thermochemical storage energy in a liquid chemical looping thermal enerrgy storage (LCL-TES) is reported. This LCL-TES cycle comprises a reduction reactor, an oxidation reactor, two reservoirs for storing the hot and cold medium and a heat recovery unit. The materials were assessed on the basis of their melting temperature, Gibbs free energy, reaction temperature and thermal storage capacity. Ellingham diagrams were used to identify regimes with a potential for application in a LCL-TES, while phase diagrams were used to identify processes which combine sensible, latent and thermochemical heat storage. Based on these criteria, the oxide of CuO/Cu_2O was found to have the greatest thermodynamic potential for use in a LCL-TES system with a total enthalpy of 404.67 kJ/mol for thermal storage. However, the high temperature of ~1200 °C and corrosive nature of molten copper and its oxides will make this cycle challenging to implement. Lead, on the other hand has a lower total enthalpy of 250.09 kJ/mol, but is molten at lower temperatures.

1. Introduction

Concentrated solar thermal (CST) power has received great attention due to its compatibility with thermal energy storage, which enables management of the variability of solar radiation at relatively low cost (Kuravi et al., 2013; Pacio et al., 2013; Pacio and Wetzel, 2013). Moreover, CST has many similar generation characteristics to conventional fossil and nuclear power generation, but with very low emissions of pollutants. The current state-of-the-art technology employed for the storage of solar thermal energy is based on the application of molten salt as a storage medium. However, decomposition of molten salt limits the upper temperature of this technology to a temperature of typically below 600 °C. Although this temperature is suitable for a steam Rankine cycle with a thermodynamic efficiency of approximately 35% (Wong, 2011; Gil et al., 2010), it is desirable to achieve higher temperatures which potentially offer a higher efficiency. A cycle temperature of greater than 600 °C requires the development of new receivers, heat transfer fluids and storage media. Therefore, it is important to evaluate the potential of other materials that can absorb and store energy at higher temperatures. The objective of this paper is to explore the performance of novel materials with a potential to meet this need.

The three main types of thermal energy storage (TES) are sensible, latent and thermochemical heat storage (Gil et al., 2010). These are not necessarily mutually exclusive but have the potential to be combined together. At present, sensible heat storage using molten salts is the most developed storage medium (Kuravi et al., 2013; Gil et al., 2010; Price, 2003; Robak et al., 2011; Yang and Garimella, 2010; Price et al., 2002; Zhang et al., 2013; Kolb, 1998). Molten salts operate in a broad temperature range between their melting point, which is typically around 200 °C, and their stability limit of approximately 600 °C. The relatively high melting temperature of molten salts results in a significant risk of solidification, which may lead to the failure of the system (Kearney et al., 2003). The need to avoid solidification is typically managed with the use of trace heating, which constitutes a significant parasitic energy loss. To avoid these challenges, liquid sodium with a melting temperature of around 98 °C has been proposed as an alternative heat transfer fluid and tested for a solar thermal power plant at de Almeria (Spain) Pacio et al., 2013. While sodium has excellent thermal and hydraulic performances, its implementation has been delayed at an industry scale at the de Almeria CSP plant due to its increased safety risk (Schiel and Geyer, 1988). Nevertheless, Sodium has since been used successfully in a solar thermal plant at Jemalong in Australia (Coventry et al., 2015). There have also been some attempts to use other liquid metals such as Lead-Bismuth and molten tin for sensible heat storage (Pacio et al., 2013). However, the low heat capacity of liquid metals in comparison to molten salts is a potential disadvantage of using these materials for sensible thermal energy storage alone.

Another method to store energy is via latent TES which stores the

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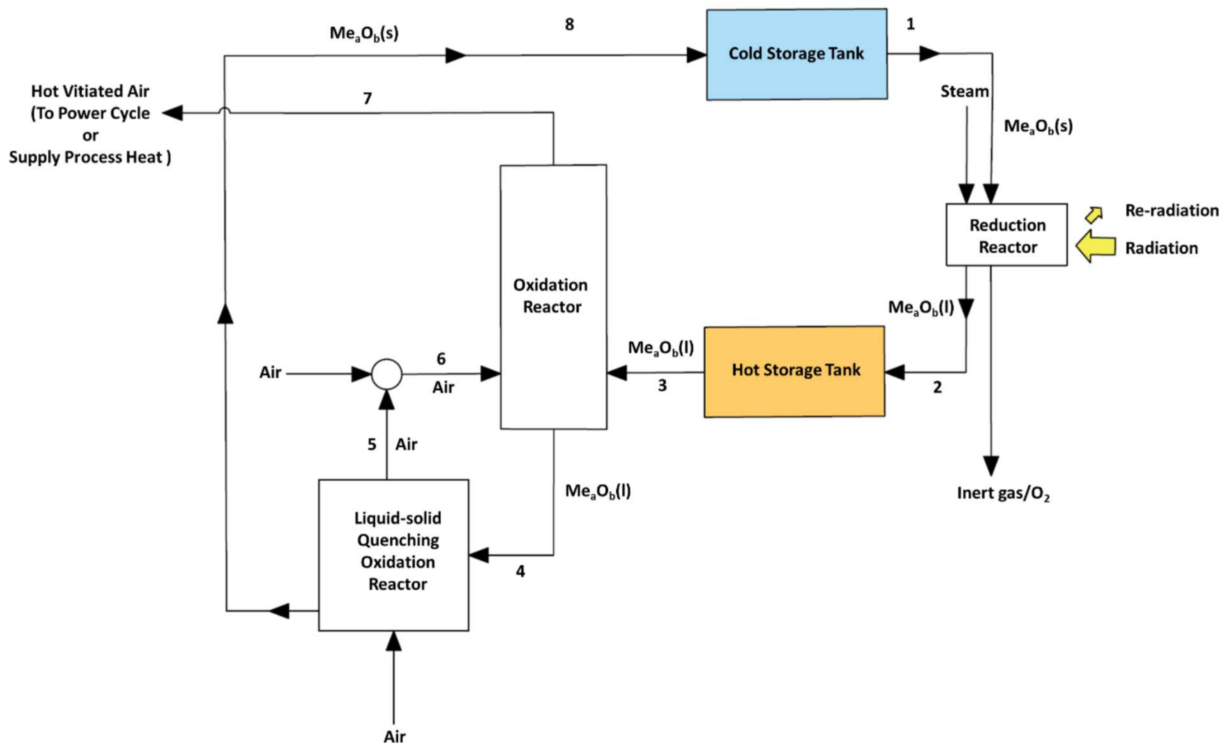

Fig. 1. Schematic representation of the key components of the proposed LCL-TES system assessed here for the liquid chemical looping with thermal energy storage of solar thermal energy as sensible, latent, and thermochemical heat and for co-production of pressurized air and oxygen. A cold storage reservoir and a hot storage tank are proposed for the storage of the cold solid metal oxide particles and the hot liquid metal oxide, respectively. The hot vitiated gas can be used for a power generation at pressure of 5–30 bar or process heat. The figure is adopted from Jafarian et al. (2017).

energy within the phase change of a material. A number of materials have been proposed previously for latent TES, such as NaCl (Mehling and Cabeza, 2007), Li_2CO_3 (Kuravi et al., 2013), $MgCl_2$ (Gil et al., 2010), LiF (Mehling and Cabeza, 2007), $NaCO_3$-$BaCO_3$/MgO (Gil et al., 2010). These offer charge and discharge at a constant temperature and a greater energy density than sensible heat. However, the change in their volume during the charge and discharge processes, together with their low thermal conductivity have, thus far, limited their implementation. Nevertheless, a number of methods are being proposed to overcome these challenges (Silakhori et al., 2014, 2015; Naghavi et al., 2015).

Thermochemical energy storage is being investigated because it offers an energy density of up to fifteen times higher than sensible heat storage and six times higher than latent heat storage for several types of materials (Abedin and Rosen, 2011). Like latent heat it also enables the heat to be stored and recovered at a similar temperature (Nagel et al., 2013), but thermochemical energy system is yet to be developed at a commercially level. The cyclic reduction and oxidation (Red-Ox) of metal oxides has been identified as a promising concept for thermochemical energy storage at a temperature range of 350–1100 °C (Wong et al., 2010; Pardo et al., 2014). The general reactions for metal oxides used for thermochemical storage are:**

$$\text{Reduction reaction:} Me_aO_b \rightarrow \left(\frac{a}{c}\right)Me_cO_d + \left(\frac{bc-da}{2c}\right)O_2 \quad \Delta H > 0, \tag{1}$$

$$\text{Oxidation reaction:}\left(\frac{a}{c}\right)Me_cO_d + \left(\frac{bc-da}{2c}\right)O_2 \rightarrow Me_aO_b \quad \Delta H < 0. \tag{2}$$

Several metals and metal oxides have been considered for the application in thermochemical energy storage. The oxide of BaO_2/BaO was first investigated by Fahim and Ford (1983). This reaction occurs at temperatures between 400 and 1027 °C for partial oxygen pressures of between 0 and 10 bar. They demonstrated that complete conversion was inhibited by mass transfer limitations and crusting of the material surface (Bowrey and Jutsen, 1978). A recent study of sixteen oxides by Wong et al. (2010), found that only BaO_2, Co_3O_4, Mn_2O_3, CuO, Fe_2O_3, and Mn_3O_4 exhibit suitable performance as TCS materials. Of these, Co_3O_4 was found to yield the best performance in terms of reversibility and energy storage density, although the consecutive cycling between the temperatures of 850 °C and 950 °C for oxidation and reduction, respectively, decreases the isentropic efficiency of TES process due to exergy destruction (Block et al., 2014). In addition, the application of solid metal oxides is presently limited to an operating temperature of approximately 1000 °C (Adanez et al., 2012; Haseli et al., 2017) because of the technical challenges associated with the sintering, softening, agglomeration of solid metal oxide in RedOx reaction. This temperature is significantly lower than the state-of-the-art in commercially available gas turbines which are currently around 1250 °C (Bhargava et al., 2007; Hunt, 2010) and potentially will reach up to 1700 °C in the future (Chyu, 2012). For these reasons, considerable effort has been invested to identify materials enabling operating temperatures of more than 1000 °C. Furtheremore, liquid metal oxides have also been proposed as an alternative solution to solid metal oxide systems (Jafarian et al., 2017).

Liquid chemical looping thermal energy storage (LCL-TES) system is a newly proposed technology based on the use of liquid metal oxides at a high temperature for both thermal energy storage and as a heat transfer medium to improve the overall efficiency of the system (Jafarian et al., 2017). The validity of the process as a potential storage medium has been assessed thermodynamically, but only for copper oxide. Therefore, there is a need to assess the potential of other metal oxides in a LCL-TES system. Moreover, the parameters that best describe the performance of a LCL-TES system are yet to be identified.

For the reasons outlined above, the objective of the present investigation is to compare the thermodynamic feasibility of alternative metal oxides for the application in a LCL-TES system for power generation using a gas turbine combined cycle, which requires the hot gas