

Hybrid strontium bromide-natural graphite composites for low to medium temperature thermochemical energy storage: Formulation, fabrication and performance investigation

A. Cammarata^a, V. Verda^a, A. Sciacovelli^{b,*}, Y. Ding^b

^a Department of Energy, Politecnico di Torino, Turin 10129, Italy

^b Birmingham Centre for Energy Storage, School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK



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ABSTRACT

Thermochemical energy storage has the potential to provide efficient, compact and long duration storage of thermal energy. Major advancements, however, are needed for such a technology to meet performance and cost targets. Here we present a study on novel composites for low to medium temperature thermochemical energy storage (< 150 °C) with an aim to maximize energy density and to understand the associated mass and heat transport phenomena. The composites were made of strontium bromide hexahydrate and natural graphite with the latter acting as a supporting matrix. We used a simple manufacturing method to fabricate the composites and experimentally characterized the performance of the materials using various methods including thermogravimetry, laser flash analysis and dynamic vapor sorption. The results showed that the composites achieved an energy density above 600 kJ/kg with the storage process occurring mostly below ~100 °C – a promising feature for domestic applications. The results also showed that the natural graphite could improve the hydration-dehydration kinetics by reducing hysteresis and a fourfold increase in the thermal conductivity could be achieved with 20% of natural graphite in the composite.

1. Introduction

Recent years have seen increased demands for effective and efficient thermal energy storage (TES) technologies for clean heat and cold supply, which currently accounts for 40–60% of final energy consumption in most of the counties [1–3]. This is driven by the needs for increasing renewable energy penetration and decarbonisation of heating & cooling, as well as harnessing waste heat/cold and peak shaving of energy networks. There are three types of TES technologies based respectively on sensible heat, latent heat and reversible thermochemical processes. Thermochemical based method has the potential to store 8–20 times more thermal energy per unit of mass of storage material than the sensible and latent heat based TES technologies, and has therefore attracted significant attention in the past decade [4–8]. However, the technology readiness level of the thermochemical storage (TCS) is still low and has multiple challenges including life span and stability of storage materials, efficient thermochemical reactors and integration and TCS system costs. These challenges have been hindering the industrial uptake of technology [9–12].

The work presented in this paper concerns TCS for domestic applications with a focus on operations at a low to medium temperature

range (50 °C–150 °C) due to safety considerations. Over the temperature range, salt hydrates are regarded as the most promising TCS materials for which numerous material systems have been proposed in the literature [13–15]. Most of them, however, are unable to meet the criteria for use in a domestic environment. N'Tsoukpo et al. carried out screening of 125 salts and showed that the most promising salts were SrBr₂·6H₂O, LaCl₃·7H₂O and MgSO₄·6H₂O [13]. Fopah-Lele and Tamba suggested that SrBr₂·6H₂O was the best candidate when an external free source of heat was available for the evaporation of water [16]. As a result, the hybrid strontium bromide was targeted in this work. Fig. 1 shows a schematic diagram using a domestic building as an example where solar thermal energy from vacuum solar panels (up to ~150 °C) and/or other renewable heat produced by a heat pump driven by electricity from wind and solar energy is stored in the TCS system.

The TCS shown in the figure is based on the reversible hydration/dehydration reaction of the targeted hydrate as discussed above. During the charge process, heat is supplied to break the chemical bonds between the salt (also termed sorbent) and water molecules (also called sorbate), resulting in the release of water in the form of H₂O vapor. The sorbate is either condensed for use in the discharge process, in the case of a closed TCS system, or released into the environment in the case of an open TCS

* Corresponding author.

E-mail address: a.sciacovelli@bham.ac.uk (A. Sciacovelli).

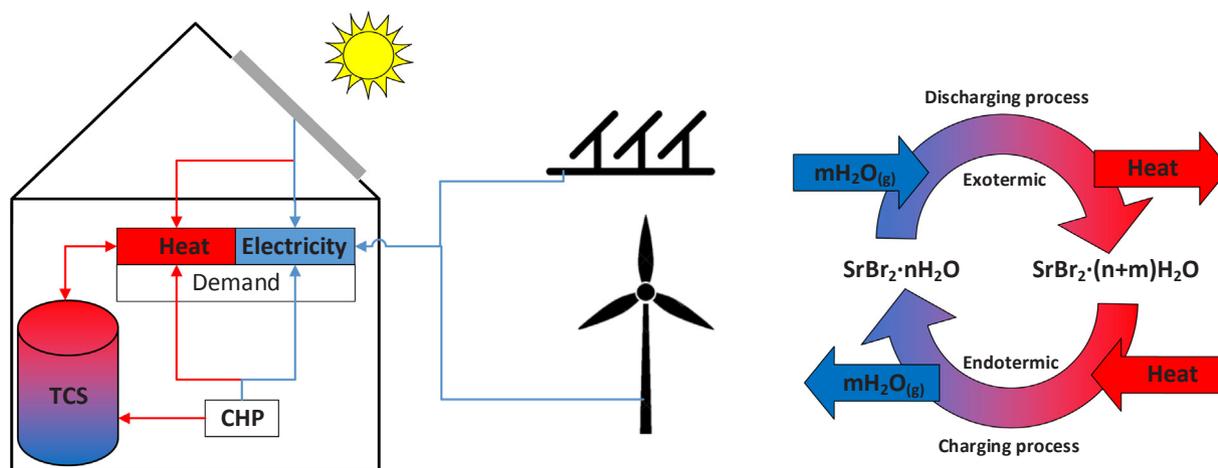


Fig. 1. A thermochemical storage (TCS) device for a household application (Left); a schematic of thermochemical reaction (hydration/dehydration) for thermal energy storage (Right).

system. The discharging process occurs through an exothermic hydration reaction when water vapor combined with the salt, releasing the stored heat. Eq. (1) illustrates the reversible reaction.



The use of pure salt hydrates as TCS materials come across a number of challenges including heat and mass transfer limitations induced mainly by structural change and shape stability of TCS materials. This is similar to the challenges in the use of pure phase materials in the latent heat storage and also chemical looping technology. The use of composite TCS materials have the potential to overcome the challenges and, as a result, a number of studies have been carried out in recent years. These studies used various salts (e.g. MgSO_4 , CaCl_2 and LiBr) in different structural materials including zeolite, silica gel and activated carbon [12,17,18]. Composite TCS containing SrBr_2 , however, remains largely unexplored, and the published studies were primarily on energy storage density [19–21] or on the performance of pure SrBr_2 at the reactor scale [8,22,23]. To our knowledge, no studies have been published on linkage between the performance and structure of the composite TCS containing SrBr_2 – the main motivation of this paper. In this work, we used natural graphite as the structural material (matrix host) for the SrBr_2 based TCS composites. A simple manufacturing processes is proposed and used to fabricate the composite. We found, for the first time, how the composite formulation affect the energy density, heat and mass transfer, and reaction kinetics. Our work investigates for the first time the links between formulation and thermal properties of TCS composites, including enhancement in thermal conductivity and specific heat, which are shown to impact significantly on total energy density.

2. Manufacturing and characterization of TCS composites

2.1. Manufacturing process

Fig. 2 illustrates schematically the manufacturing process of TCS composites. Natural carbon graphite supplied by Inoxia Ltd UK with the following composition 98.6% Carbon, 0.05% Sulphur, 0.05% Nitrogen, 0.8% ash, 0.3% Volatile and 0.3% Moisture was used; from the previous composition and from the molecular weight of H_2O we estimated a 0.27% of O content in the graphite. The graphite was initially dried in oven at 150°C for 12 h to remove any trace of moisture, as depicted in Fig. 2. A water solution of strontium bromide (SrBr_2 , chemical reagent grade, Aldrich) was then prepared using distilled water. The amounts of water and salt were set in such a way to achieve a salt content of 40% or 80% (by mass) in the final dry TCS composites. A wet impregnation

process was then followed to fabricate the TCS composites, which involved the addition of the salt solution at a slow and constant rate to the graphite particle bed with the bed being stirred. The solution addition process was carefully controlled so that the particle bed appeared to be dry macroscopically with the salt solution fully drawn into the intraparticle pores of the particle bed. This resulted in a wet mass of the composite, which was then placed in an oven to remove the water in the matrix and dehydrate the salt. A minimum drying temperature of 200°C was chosen to ensure full dehydration of the salt. Finally, the dehydrated TCS material was then shaped using die-plunge device in a Lloyd LS100Plus testing machine to give circular tablets of 13 mm diameter and a thickness between 1 and 2 mm; see Fig. 3.

2.2. Characterization of TCS composites

2.2.1. Scanning electron microscopy (SEM)

The TCS materials were imaged using a Hitachi TM3030 scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDX); A 5 kV accelerating voltage was used for the observations whereas the EDX analysis was carried out at 15 kV. The TCS samples were coated with a 5 nm layer of gold using a Quorum Q150T sputter coater in order to avoid the charge-up phenomenon.

2.2.2. Specific surface characterization

Nitrogen physisorption was performed using a Micromeritics ASAP 2020 plus. For doing so, TCS composite samples of 0.4–0.5 g were dried and degassed at 250°C for overnight before measurements to remove moisture and any gas adsorbed. Both adsorption and desorption isotherms were obtained using nitrogen as gas adsorbate and an equilibrium time of 5 min was adopted at each relative pressure p/p_0 . Specific surface area was then derived from the isotherms using a multipoint Brunauer–Emmett–Teller (BET) method.

2.2.3. Differential scanning calorimetry

The heat of reaction, and the onset and peak temperatures of the TCS composite were measured with a differential scanning calorimeter from Mettler-Toledo (DSC2+) equipped with a robotic sampling unit for automatic measurements. For such measurements, samples of ~ 10 mg obtained from the TCS composites were first placed in closed platinum crucibles and then positioned in the robotic sampling unit of the DSC. The DSC measurements then took place by heating the sample up from 20°C to 300°C at a heating rate of $5^\circ\text{C}/\text{min}$ (with a 10 min isothermal holding period at the initial/final temperature) under a constant N_2 flow of 50 ml/min. The specific heat of the TCS composites was obtained by comparing DSC signal (heat flux) with the DSC signal

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