



Development and characterization of silica gel–LiCl composite sorbents for thermal energy storage



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HIGHLIGHTS

- Silica gel–LiCl composite sorbents were prepared for thermal energy storage.
- Salt concentration and pore volume are key parameters to find suitable sorbent.
- SLi30 was determined to be the most appropriate sample.
- The characteristic curves of the sorbents should be divided into three sections.
- Cold and heat storage densities of the sorbents were identified via calculation.

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ABSTRACT

The development of renewable energy conversion systems closely depends on the progress in efficient thermal energy storage (TES) processes. Recently, sorption thermal energy storage (STES) is perceived as a promising option for TES owing to the advantages of high energy storage density, long-term heat preservation ability and flexible working modes. This study aims to find a suitable silica gel–LiCl composite sorbent for the application of STES via the optimization of some key parameters, among which, the mass concentration of the impregnating solution and the pore structure of the matrix are most important. According to the measured sorption isobars and the pore volumes, it could be concluded that the SLi30 sample is the most appropriate composite as it offers the largest water uptake under typical working conditions for closed SETS systems and meanwhile it is free of the worrying issue of solution carryover. Another advantage of the composite sorbents is that complete water desorption can be reached at relatively low temperatures, from 60 to 100 °C. The Dubinin–Astakhov (DA) equations derived from the Polanyi theory were used to simulate the sorption properties of five sorbents. The calculation results showed that the energy densities for the composite sorbents have been remarkably improved as more hygroscopic LiCl was added into the silica gel matrix. The SLi30 sample could achieve a cold storage density of 108 kWh/m³ and a heat storage density of 163.6 kWh/m³ at a desorption temperature of 80 °C. Overall, the results demonstrate that the prepared silica gel–LiCl composite sorbents in this paper are good candidates for low-temperature driven STES systems.

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1. Introduction

Thermal energy storage (TES) plays an important role in the process of converting renewable energy by decreasing the mismatch between the supply side and the demand side, to improve the performance and reliability of the energy systems. The increasing use of solar energy closely depends on the development of reliable

and economically viable TES systems. Therefore, burgeoning attention has been drawn to find suitable solutions for TES recently.

Methods of TES can be generally divided into three groups: sensible heat storage, latent heat storage and thermochemical heat storage (N'Tsoukpoe et al., 2009; Wang et al., 2012b). Sensible heat storage is based on storing thermal energy by the temperature difference of the storage medium (e.g., water, sand and rock), with water being the most common and cheapest option. Latent heat storage relies on the energy released or absorbed during a phase change process of a material. These traditional heat storage technologies suffer major disadvantages including the inability to

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be downsized economically, low energy densities and for consideration in long-term storage, unacceptable energy losses.

Thermochemical sorption processes have been extensively researched for use in refrigeration and heat pump systems (Dutour et al., 2005; Li et al., 2010). In sorption thermal energy storage (STES) processes, heat is stored by breaking the binding force between the sorbent and the sorbate in terms of chemical potential. STES cycles could provide the following features (Yu et al., 2013): (1) the desorption heat required is higher than that associated with the evaporation heat of pure sorbate (such as water), leading to a high energy density, in theory, only next to chemical reaction. (2) A sorption process will not occur until the sorbent contacts with the sorbate, meaning that it stores energy as chemical potential. The potential does not require insulation and would not degrade with time, yielding a great opportunity for using sorption processes in long-term TES application. (3) STES systems can offer both cold storage function and heat storage function, exhibiting more flexibility than traditional sensible and latent systems.

Due to all the listed features, research efforts have been focused on the goal of identifying appropriate sorption materials for STES. With consideration of non-toxicity, low costs and availability, water has always been chosen as the most feasible sorbate in open and closed systems and it could be coupled with a number of sorbents. Zeolite/H₂O (Dawoud et al., 2007; Hauer, 2002, 2007, 2011; Jänchen and Stach, 2012) and silica gel/H₂O (Jaehnig et al., 2006; Tahat, 2001) are the most studied working pairs. Hauer (2007) reported an successful large-scale open sorption system with 7000 kg zeolite (13 ×), which was installed in a school in Munich and connected to the local district heating network, achieving a heat storage density of 124 kWh/m³. Jaehnig et al. (2006) developed several generations of prototypes in a series of studies and experimentally achieved a material storage density of 50 kWh/m³ based on the volume of silica gel. The main drawback for zeolite/H₂O is the high desorption temperature – above 150 °C or even 200 °C is required to complete a sufficient regeneration. Though silica gel/water could be well desorbed by a heat source temperature lower than 100 °C, the low storage density limits its application in closed STES systems.

In the last decade, hydration reactions of salt hydrates with water have been proposed for TES with their theoretic high storage densities. Among all the hygroscopic salts, MgCl₂/H₂O (Zondag et al., 2013), Na₂S/H₂O (Lammak et al., 2004), SrBr₂/H₂O (Mauran et al., 2008) and MgSO₄/H₂O (Van Essen et al., 2009) have been identified as potential candidates. Though hydration reactions possess excellent storage potential based on the analysis on the material level, applying these materials in actual systems requires further considerations, owing to some heat and mass transfer issues related with solution carryover, swelling and agglomeration phenomena. Impregnating the salt into a porous structure could solve such problems in some extent. This family of composite sorbents, called “composite salt porous matrix” (CSPM) (Aristov, 2007; Gordeeva and Aristov, 2012), has been adopted for sorption cooling, heat pump and energy storage applications. It involves two-component sorbents: one component is a host matrix (silica gel, zeolite, expanded vermiculite, etc.), the other is a hygroscopic salt (LiCl, CaCl₂, MgCl₂, MgSO₄, etc.) placed inside the matrix pores. Hongois et al. (2011) prepared a zeolite/MgSO₄ composite (ZM15) for low-temperature heat storage applications. An energy density of 166 kWh/m³ was obtained with an inlet air RH of 50% in an open cycle. The water sorption properties of the silica gel–CaCl₂ composite have been extensively studied by Aristov et al. (Aristov et al., 2006, 1996a, 1996b) and its potential for TES has been investigated by Wu et al. (2007) and Zhu et al. (2006) in an open STES system.

One of the most crucial problems needed to be paid attention is the carryover of deliquesced salt solution droplets, which has been

ignored by some previous studies. Although the porous matrix could hold some amount of solution with its pore space, the internal pore volume is limited and the carryover is still the most worrying issue – especially under conditions when the water uptake is great. Gong et al. (2010, 2011, 2012) suggested an additional forced deliquescence treatment in a constant temperature and humidity chamber with a high humidity (90%). Whereas, the obtained mass fraction of salt in the composite was only 13%, since most of the salt content was removed after the treatment. To prevent the carryover from happening, another possible approach is to design a suitable sorbent according to the designed conditions, by optimization of the salt content and remaining pore volume after impregnating. In this study, some key parameters regarding the development of a serial of silica gel supported lithium chloride composite sorbents were discussed. The appropriate impregnation concentrations were determined from the water uptake which can be held inside the pores of silica gel. The heat and cold storage performances of the composite sorbents were evaluated theoretically with thermodynamic equations derived from the Polanyi approach.

2. Experimental

2.1. Materials

Two types of silica gels with different parameters, namely type A with an average pore diameter of 2–3 nm and type C with an average pore diameter of 8–10 nm, were applied in this study to find a suitable matrix for lithium chloride. The size of the silica gel grains was 2–3 mm. First, the silica gel was dried at 120 °C in an oven to drive possible remaining water out of it. The dry silica gel was then immersed into aqueous LiCl solutions with varied mass concentrations in the range of 10–40 wt% at an ambient temperature of about 25 °C for 12 h, which is sufficient to make the salt well distributed inside the pores of silica gel. Instead of a sieve, a vacuum filter including a vacuum pump beneath the filter was used to separate the samples and the solutions, because the vacuum filtering process could remove not only the salt solution between the particles but also the solution clung on the surface of the particles in some extent. After that the samples were dried again in the oven at 120 °C until the variations of their weights were found nil. The salt contents in the composites were determined by weighing dry samples before and after impregnation.

2.2. Characterization methods

Specific surface areas and porous characteristics of the composites were measured through the standard nitrogen adsorption/desorption measurements using a Micromeritics ASAP2020 gas adsorption analyzer. The sorption isotherms were implemented at 77 K. The specific surface areas were calculated using the conventional BET (Brunauer–Emmett–Teller) method. The pore size distributions were obtained based on the N₂-desorption branches of the isotherms using the BJH (Barret–Joyner–Halenda) method.

The experiment setup which was used to measure the water sorption characteristics of the composite sorbents was built based on a thermogravimetric instrument named Rubotherm magnetic suspension balance. This type of thermogravimetric instrument has been adopted in many laboratories around the world (Riffel et al., 2011; Wang et al., 2012a; Zhong et al., 2007) as a precise and convenient solution to investigate sorption properties (isobars and isotherms) of varied kinds of sorbents. The schematic and photo of the Rubotherm magnetic suspension balance in Shanghai Jiao Tong University are presented in Fig. 1. The most distinctive feature of this balance is that instead of hanging directly under the balance,

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