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Study on consolidated composite sorbents impregnated with LiCl for thermal energy storage

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ABSTRACT

$LiCl/H_2O$ shows a great potential for sorption thermal energy storage with its large water sorption capacity. However, as a highly hygroscopic salt, LiCl is likely to turn into liquid solution when it contacts with water vapor. A new type of consolidated composite sorbent was developed, by using activated carbon (AC) as a porous host matrix to carry LiCl, mixing with expanded natural graphite treated with sulfuric acid (ENG-TSA) to increase heat transfer and adding silica solution (SS) as a binder to enhance mechanical strength. Samples with different densities and varied mass ratios between different elements were prepared and related characteristics including equilibrium water uptake, thermal conductivity, TGA/DSC simultaneous thermal analysis and kinetic performance were investigated. Results reveal the existence of an obvious sorption plateau corresponding to formation of $LiCl \cdot H_2O$, as well as two sharp increase of water uptake related to hydration reaction and three-phase deliquescence processes respectively. Activated carbon is a better choice of matrix compared with silica gel, with a water uptake up to 0.97 g/g at 30 °C and 1660 Pa. It is proved that among the four elements in the consolidated composite (AC, LiCl, ENG-TSA, silica solution), LiCl is responsible for almost all the water uptake effect. Addition of other elements do not influence the equilibrium water uptake of LiCl. Variation of bulk densities from 462 to 820 kg/m^3 displays thermal conductivities from 2.0 to 2.83 W/(m K), improving that of loose-packed AC–LiCl composite by at least 14 times.

1. Introduction

Currently available thermal energy storage (TES) systems used for heating or cooling of buildings mainly rely on sensible heat storage using water, rock or concrete, and latent heat storage using ice or paraffin wax phase change materials (PCMs). In the recent decade, another emerging technology proposed for TES is thermochemical energy storage using reversibly thermochemical processes to store heat in the form of chemical potential. As an important type of thermochemical processes, sorption processes have been extensively studied for the possibility of being applied in the area of TES [1,2]. Research interests in sorption TES technology is due to the advantages of substantially high energy storage densities, the ability to preserve energy for long periods with limited heat losses and combing cold storage and heat storage functions in one system [2]. Water is always the preferred choice of working vapor (sorbate) with its safety and low cost. Typical water sorbents include solutions of hygroscopic salts like LiCl [3,4], which absorb water in their bulky solution phase, zeolite [5] or silica gel [6], which adsorb the sorbate on the surface of their porous structure and salt hydrate materials like $MgSO_4$ [7], which have solid/gas thermochemical sorption reactions with the sorbate.

Compared with traditional water sorbents like silica gel and zeolite, thermochemical sorption processes between salt hydrates and water vapor seem more promising due to their higher theoretic storage densities. Among all the hygroscopic salts, $MgCl_2$ [8], Na_2S [9], $SrBr_2$ [10,11] and $MgSO_4$ [7] have been identified by different researchers as potential candidates. Usually, the products of hydration reactions of these salts are assumed to be hydrates with more crystal water molecules. However, a severe problem for these hygroscopic salts is forming of saturated solution at high relative humilities. This process is called deliquescence, which is defined as a first order phase transformation of the solid to a saturated solution when the relative humidity (RH) reaches a certain threshold value, namely, the deliquescence relative humidity (DRH) [12]. The concepts of RH and DRH can also be applied to closed systems, by defining RH as P/P_{sat}, in which P is the equilibrium sorption pressure and P_{sat} is the saturated vapor pressure at the same temperature. Forming of liquid solution on the surface

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Nomenclature

AC	activated carbon
ALi40	activated carbon–LiCl composite prepared in 40 wt% of LiCl solution
DRH	deliquescence relative humidity (%)
ENG-TSA	expanded graphite treated with sulfuric acid
ES	mixture of ENG-TSA and silica solution
ESALi	consolidated composite sorbent prepared with ES and ALi40
P	pressure (Pa)
P_{sat}	saturated pressure (Pa)
R	gas universal constant (J/mol K)
RH	relative humidity (%)
SLi40	silica gel–LiCl composite prepared in 40 wt% of LiCl solution
SS	silica solution
T	temperature (°C)
TES	thermal energy storage
W	water uptake (g/g)
Greek symbols	
ΔG	Gibbs free energy (kJ/kg)

of salt particles and other factors like swelling and agglomeration phenomena may cause severe mass transfer barriers thus leads to low levels of charging and discharging power. Though hydration reactions possess excellent storage potential based on the analysis on the material level, low output power remains the main challenge in developing compact thermochemical TES systems.

The DRH values for LiBr (7% at 30 °C), LiCl (11% at 30 °C) and $CaCl_2$ (29% at 30 °C) are quite low, meaning that it is more likely for them to form liquid salt solutions directly in most cases. Hence, these three salts are often applied in liquid/gas absorption cycles. In fact, if the desorption temperature is high enough to generate the solution to its crystallized state or even anhydrous state, the sorption process could be seemed as a three-phase process, during which the solid crystal could be completely turned into liquid solution [3,13]. Yu et al. [3] carried out a theoretical analysis on the three-phase sorption cycle for thermal energy storage. Results showed that appearance of the three-phase sorption/desorption process could extensively enhance the storage densities and LiCl/H_2O was identified as the best choice for both cold storage and heat storage, with cold storage density of 519 kWh/m^3 and heat storage density of 668 kWh/m^3 based on the volumes of salt solutions. This analysis has revealed the potential to use LiCl/H_2O for sorption TES, whereas, implementation of the cycle faces severe challenges when dealing with liquid solutions after water sorption, owing to the highly hygroscopic feature of LiCl.

To improve the water sorption kinetic performance for these hygroscopic salts, composite materials are usually proposed by impregnating salt in the pore space of a porous matrix, the porous structure is conductive to water–salt sorption interactions with the high specific surface area and is able to contain some amount of liquid solution with its internal pore volume. Since Aristov et al. [14–16] first introduced the concept of selective water sorbents, numerous combinations of salts with porous matrices have been raised up, such as silica gel–$CaCl_2$ [17–19], silica gel–LiCl [20,21], zeolite 13X–$CaCl_2$ [22], zeolite 13X–$MgSO_4$ [23], wakkanai siliceous shale (WSS)–$CaCl_2$ [24]. In terms of the porous matrix, adding of hygroscopic salts greatly increase the water uptake quantities; in terms of the salts, dispersing of the salt particles in porous matrix could improve the sorption kinetics.

Realization of good sorption performance also relies on the heat transfer conditions in the sorption bed. Consolidation of sorbent pellets with expanded graphite have usually been employed for improving heat conductivity [25,26]. Recently, compressed expanded graphite treated with sulfuric acid (ENG-TSA) was reported by Wang et al. [27] to have a maximum thermal conductivity of 337 W/(m K) at a density of 831 kg/m^3. Wang et al. [28] also prepared consolidated composite sorbents with AC and ENG-TSA and obtained a highest thermal conductivity of 34.2 W/(m K) with a high concentration of ENG-TSA.

The purpose of this study was to search and prepare suitable consolidated host matrices for the LiCl salt for use of sorption TES. Activated carbon was chosen as the porous matrix to hold the LiCl salt. ENG-TSA was added to enhance the thermal conductivity. Silica solution was used as a binder between ENG-TSA and activated carbon particles. The most suitable matrices should have optimized heat and mass transfer properties at the same time. So important parameters such as water sorption characteristics, thermal conductivity, TGA/DSC simultaneous thermal analysis and kinetic performance were investigated for different matrices.

2. Development of consolidated sorbents

2.1. Choice of host matrices

As mentioned above, considering the forming of liquid solution, it is necessary to find a porous matrix to offer a large surface and internal pore volume for the interaction between LiCl and water vapor. The most frequently used matrix is silica gel due to its high hydrophilic properties. In our previous work [21], mesoporous silica gel with an average pore diameter of 8–10 nm was applied to confine LiCl. The composite was prepared by directly impregnating dried silica gel particles in LiCl solutions. According to the water uptake and sorption kinetics, silica gel seems to be an appropriate matrix. Whereas, some crucial notes should be underlined for the silica gel–LiCl composite sorbents. First, silica gel particles are quite frail when contacting with liquid water or salt solution, leading to the consequence that particles turn into powders after several cycles. Second, the silicon-based structure determines that the thermal conductivity of silica gel is poor, often lower than 0.1 W/(m K) for a packed bed. So it is necessary to keep on looking for more practical matrices. Activated carbon has advantages like large internal surface area and high mechanical stability when it is exposed to liquid and vapor water. Moreover, the thermal conductivity of activated carbon itself is higher than those of zeolite and silica gel [29]. Conventionally, activated carbon is regarded as hydrophobic, especially at low relative pressures in closed adsorption systems. Recently, some researchers [29–31] have intended to modify the water sorption characteristic of activated carbon by impregnating hydrophilic water sorbents in the internal pore space. Huang et al. [30] obtained hydrophilic activated carbon by immersing silica into the mesopores and macropores of activated carbon but still the improvement on water uptake was not enough. Tso and Chao [29,31] developed composite adsorbents by soaking activated carbon in sodium silicate solution firstly and then in $CaCl_2$ solution. The water uptake was greatly improved yet the pore volume was sharply decreased by impregnating silica, whose contribution to the water uptake could be neglected compared