Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

Composite sorbents "Li/Ca halogenides inside Multi-wall Carbon Nano-tubes" for Thermal Energy Storage

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A B S T R A C T

Sorption method of Thermal Energy Storage (STES) is a promising technology towards efficient use of solar energy. Materials based on hygroscopic salts and their hydrates have a high potential for STES in term of energy storage density. This work addresses the novel composite sorbents based on Multi-Wall Carbon Nanotubes (MWCNT) impregnated with three hygroscopic salts selected for STES. The paper consists of three parts: (1) analysis of operating conditions of two selected STES cycles, namely long-term (seasonal) heat storage for the regions with moderate cold climate (LT), and short-term (daily) heat storage in winter for areas with relatively warm climate (ST); (2) preparation of the Salt/MWCNT composites (salt=CaCl$_2$, LiCl, and LiBr) adapted to these cycles, and study of water and methanol sorption on these materials; and (3) evaluation of heat storage capacity of the new sorbents and feasibility of the selected STES cycles. The results obtained show that the working pair "LiCl/MWCNT – methanol" appears to be the most advantageous for the LT cycle, while "LiCl/MWCNT – water" is the best for the ST cycle. The heat storage capacity of LiCl/MWCNT under conditions of the considered cycles reaches 1.6 and 1.7 kJ/g (or 445 and 470 W h/kg) with methanol and water, respectively, and exceeds the appropriate values for common and innovative adsorbents suggested for STES. This demonstrates the great potential of the new composites for STES and promotes the broader implementation of this emerging technology.

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1. Introduction

With the diminishing reserves of fossil fuels, the increasing energy demand and the greenhouse gas emissions rise, renewable energy, the main of which is solar energy, has gained more and more attention. Whilst this source is inexhaustible, the main barrier to its successful implementation is a mismatch between the solar energy income and the heat/cold demand [1,2]. This urges researchers to look for new materials for the Thermal Energy Storage.

Four ways were suggested for Thermal Energy Storage [3]: as sensible [4,5], latent [6,7], sorption [8,9] and chemical heat [10]. The Sorption method of Thermal Energy Storage (STES) offers the important benefits in comparison with sensible and latent heat storage: 1) larger Heat Storage Capacity (HSC); 2) possibility to

vary the temperature potential of released heat [11]; and 3) negligible heat losses during the storage phase [9,12]. STES includes two stages, namely the heat storage (charging), and the heat release (discharging). The heat to be stored is used to carry out endothermic desorption of the working fluid from sorbent. On the heating demand, the stored energy is released when the exothermic sorption occurs. Water is mainly considered as a sorbate due to its environmentally friendly properties and large heat of sorption. Methanol and ammonia can also be used, especially if the environment temperature is below 0 °C [9].

The main criteria for selection of the proper solid sorbent for STES are: 1) high HSC; 2) low charging temperature; and 3) high temperature level of the released heat. A large number of sorbents are currently considered for STES, both traditional (silica gels [12], zeolites [13,14], etc.), and innovative (AlPOs and SAPOs [15,16], metal-organic frameworks MOFs [17–19], Composites "Salt in Porous Matrix" (CSPMs) [20–23]). Silica gels are characterized by low charging temperature ($<$ 100 °C). Their drawbacks are the low HSC obtained in real systems (50 kW h/m^3 as against a theoretical value of 200–300 kW h/m^3) and not sufficient temperature lift [12]. Zeolites possess stronger affinity towards water vapour and allow high discharging temperature ($>$ 55 °C at income air temperature of 20 °C) [14]. The main shortcoming of zeolites is

Nomenclature

C	content, wt%
ΔH_{ads}	heat of adsorption, kJ/mol
ΔF	adsorption potential, kJ/mol
ΔL	heat of condensation, kJ/mol
M	molar mass, g/mol
m_0	mass of dry sorbent, g
N	amount of water(methanol) adsorbed, mol/mol
P	pressure, mbar
P_0	saturation pressure, mbar
S_{sp}	specific surface area, m^2/g
T	temperature, °C
V_{sp}	specific pore volume, cm^3/g

V_{calc}	calculated pore volume, cm^3/g
w	uptake, g/g

Subscripts

ads	adsorption
c	condenser
ch	charging
dis	discharging
ev	evaporator
s	sorptive
salt	salt
sp	specific

their high charging temperature $T_{ch}=160–250$ °C. AlPOs and SA-POs are characterized by intermediate affinity to water and demonstrate acceptable temperature lift at moderate charging temperature of 75–140 °C, and a higher HSC of 200–240 W h/kg [15]. MOFs, specifically MIL-101 and MIL-125-NH$_2$, possess very large HSC of 350–680 W h/kg and require low charging temperature of 70–80 °C [18,19]. Their key drawback is too weak affinity to water, which results in low temperature lift. The CSPMs were first suggested for STES in ref. [20] and called Chemical Heat Accumulators. Now the CSPMs are widely being studied and used for sorptive transformation and storage of low temperature heat [8,22–30]. Large number of hygroscopic salts are suggested as an active component of the CSPMs, namely CaCl$_2$ [15,20,28], Al$_2$(SO$_4$)$_3$ [21], MgSO$_4$ [23,27,28], MgCl$_2$ [28,30], LiBr and CaNO$_3$ [28]. CSPMs are characterized by high maximum (charged at relative humidity 85–90%) HSC of 200–1200 W h/kg, suitable temperature lift at moderate charging temperature, and wide variability of the sorption properties [25,31]. Due to these benefits, CSPMs are shown to be advantageous for STES [1,29].

Thus, adsorbents with weak affinity to working fluid can be charged at low temperature, but ensure a low temperature level of released heat. On the contrary, those with strong affinity provide large temperature lift, but require high charging temperature. Consequently, a compromise between the charging temperature and the temperature lift has to be found, taking into account operating conditions of the particular STES cycle. In other words, the adsorbent should ensure the temperature lift, suitable for the consumer, at the charging temperature of available heat source.

This paper addresses the intent design of new sorbents, which properties match well the operating conditions of particular STES cycles, as suggested in [25,32]. This concept of "optimal adsorbent" allowed the development of a number of advanced CSPMs specialized for various adsorption cycles [24]. Here we apply the same approach to intently synthesize new CSPMs adapted to selected STES cycles.

Two important STES cycles are selected for detailed consideration in this paper. The former cycle, designated as LT, is deemed to be for long-term or seasonal heat storage in regions with moderately cold winter, so that the heating demands can be, at least partially, compensated by the excess of solar heat stored in summer. The latter cycle (ST) is for short-term (daily) heat storage in winter in regions, where the solar thermal energy during day time is intense enough to be stored, and then used for heating at night, when the ambient temperature falls lower the comfortable level.

Firstly, based on the analysis of operating conditions of these cycles, the requirements to the properties of desirable adsorbent are formulated. Proper salts for the new CSPMs were selected on the base of thermodynamic data available in the literature for reaction between inorganic salts and water/methanol vapour. Multi-Wall Carbon Nano-Tubes (MWCNT), which is a novel material promising for adsorption technologies due to its extremely large and variable pore volume, was used as a matrix that hosts the selected salt, as it was first suggested in [33,34] for calcium chloride. The composite "CaCl$_2$/MWCNT" was shown to possess an enhanced water/ammonia sorption capacity of 0.9–1.4 g/g. CaCl$_2$ was shown to react with water vapour forming crystalline hydrates CaCl$_2$.NH$_2$O ($N=1$, 2) and then the aqueous salt solution. Furthermore, the mixing CaCl$_2$ with MWCNT prevents the salt agglomeration. That is very beneficial for STES because it increases both the adsorption rate and salt conversion to the hydrated state [33]. The texture, phase composition, water and methanol sorption equilibrium of the new composites are comprehensively studied in the paper. On the base of this analysis, the potential of the new sorbents is evaluated for the LT and ST cycles.

2. Analysis of the cycles operating conditions

The operating conditions of a STES cycle are determined by four temperatures, namely, the required temperature of recovered heat (T_{dis}), the temperature of heat available for evaporation (T_{ev}) during the discharge stage, the temperatures of available heat source (T_{ch}) and heat sink (T_c) during the charge stage (Fig. 1).

For both LT and ST cycles, the required temperature of released heat $T_{dis}=35$ °C (Table 1, Fig. 1), which could be used in the warm floor or air conditioning systems [35]. The charging temperature T_{ch} is 75 °C (Table 1), which can be provided by modern flat solar collectors for both LT cycle in summer and ST cycle in winter.

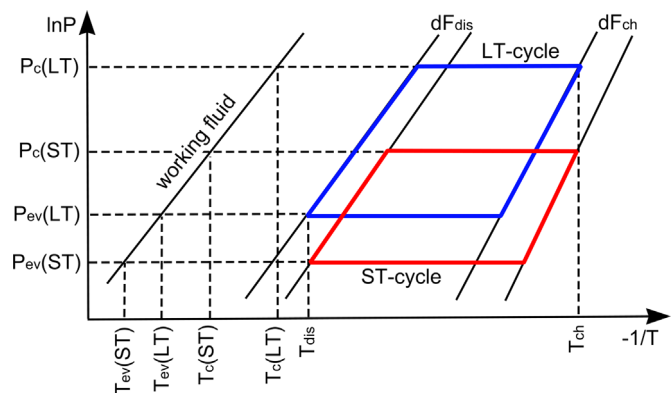The ambient air can be used as a heat source for evaporation

Fig. 1. Operating conditions of the LT and ST cycles (bold lines).

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