THE WORKING PAIR "LICL/MULTI-WALL CARBON NANO-TUBES" - WATER FOR THERMAL ENERGY STORAGE: DYNAMICS INVESTIGATION

I.S. Girnik, A.D. Grekova

Boreskov Institute of Catalysis, Russia, Novosibirsk, Ac. Lavrentiev av. 5, 630090

E-mail: girnikis@gmail.com

РАБОЧАЯ ПАРА "LiCl/МНОГОСЛОЙНЫЕ УГЛЕРОДНЫЕ НАНОТРУБКИ» - ВОДА ДЛЯ ЗАПАСАНИЯ ТЕПЛОВОЙ ЭНЕРГИИ: ИССЛЕДОВАНИЕ ДИНАМИКИ

И.С. Гирник, А.Д. Грекова

Институт катализа им. Г.К. Борескова,

Россия, Новосибирск, пр. Академика Лаврентьева 5, 630090

E-mail: girnikis@gmail.com

Аннотация. Сорбционное запасание тепла (СЗТ) – одна из перспективных технологий для эффективного использования возобновляемых источников энергии. Композитные материалы типа «Соль в пористой матрице» представляют интерес для СЗТ, так как демонстрируют высокие значениями запасающей способности. Недавно для СЗТ был предложен новый сорбент на основе хлорида лития и многослойных углеродных нанотрубок «LiCl/(МУНТ)», характеризующийся запасающей способностью 1,7 кДж/г. Новый материал представляет собой порошок, что затрудняет его загрузку в теплообменник. Данная работа посвящена: 1) формованию нового композита с использованием поливинилового спирта в качестве связующего; 2) исследованию сорбционного равновесия гранулированного композита с парами воды и оценка его запасающей способности; 3) изучению динамики сорбции воды в условиях суточного цикла СЗТ на небольшом, но репрезентативном фрагменте реального оребренного плоского теплообменника; 4) оценке удельной мощности для стадий запасания и высвобождения тепла. Было показано, что динамические кривые сорбции воды подчиняются экспоненциальному закону с характерным временем τ = 90-300 с. При конверсии 0,8 удельная мощность для стадии выделения тепла варьируется в диапазоне 2,9-4,1 Вт/г, для стадии запасания тепла – 9,7-9,8 Вт/г. Высокие значения удельной мощности наряду с большой запасающей способностью нового композита демонстрируют перспективность упомянутого материала для СЗТ.

Introduction. With the depletion of fossil fuels and the growing environmental pollution, the requirement for technologies utilizing the renewable and waste heat energy sources is rising immensely [1]. Wider dissemination of these technologies is hampered by the intermittent character of renewable energy supply. Thermal energy storage (TES) is a promising method to improve the flexibility of renewable energy systems and to reduce the energy consumption. Among different ways of thermal energy storage the sorption heat storage (SHS) has gained large interest due to its high heat storage density and negligible heat losses during the storage phase [2]. The SHS consists of two stages, namely the heat storage (charging during endothermic desorption), and the heat release (discharging during exothermic sorption). Water is considered as the optimal adsorbate for SHS because it is characterized by large sorption heat, completely nonflammable, thermally stable and ecologically benign. The development of new advanced sorbents is prerequisite for further SHS elaboration. The

composites "salt in porous matrix" (CSPM) suggested in [3] are promising sorbents for SHS due to their high Heat Storage Capacity (HSC) and tunable sorption behavior. Recently, the composite "LiCl inside Multi-Wall Carbon NanoTubes" (LiCl/MWCNT) with high heat storage capacity of 1.7 kJ/g under conditions of daily heat storage cycle (DS), has been suggested for SHS [4]. However, the new material is a powder, which makes it difficult to load it into the heat exchanger. This paper addresses: 1) shaping the new composite as grains using polyvinyl alcohol as a binder 2) studying of sorption equilibrium for pair LiCl/MWCNT/PVA –water, 3) investigating of water sorption dynamics on the LiCl/MWCNT/PVA under conditions of the DS cycle (Table 1) on small, but representative fragment of real finned flat-tube heat exchanger.

Table 1

Operating conditions of the DS cycles

Cycle	Temperature of discharging,°C	Temperature of evaporation,°C	Temperature of charging,°C	Temperature of condensation,°C
DS	35	5	75-85	15

Materials and methods. The solution of polyvinyl alcohol (15 wt.%) was used as a binder. Multi-walled carbon nanotubes were mixed with a binder solution in a ratio of 3 g of tubes - 20 ml of solution. Then the paste was extruded through a syringe extruder. The extrudate was dried at room temperature for 12 hours and at 120 °C for 2 hours. Then the sample was slowly heated in an argon flow up to 400 °C and calcined for 4 hours. The resulting sample was ground and sieved to obtain fractions with a size of 0.4-0.5 mm and 0.8-0.9 mm. The granules were impregnated with a solution of lithium chloride by the dry impregnation method. The concentration of salt in the sample reached 55 wt.%. Sorption equilibrium with the composite was investigated by thermogravimetric technique. Water sorption dynamics was studied under operating by the Large Temperature Jump (LTJ) method [5].

Results and discussion. Isotherms of water sorption on LiCl(55)/MWCNT/PVA are S-shaped curves with the steps of uptake that can be attributed by the complexes $LiCl \cdot nH_2O$ ($n = 1, 2$) formation. Sorption capacity of the composite exceeds 0.7 g/g that is profitable for SHS. Under conditions of heat release stage the material sorbs 0.65 g/g. During heat storage stage regeneration temperature T= $85^{\circ}C$ is enough to desorb approximately all sorbed water. The HSC of the composites is estimated as HSC = $\Delta w \Delta H_{ads}$. So, the value of HSC obtained for the new composite reaches 2.1 MJ/kg are superior to appropriate values (0.1–0.9 MJ/kg) reported for the adsorbents proposed for SHS, like silica gel, zeolites, AlPO-18 and SWS-1L [2].

The kinetic curves (Fig. 1) of water sorption on grains 0.8-0.9 mm and 0.4-0.5 mm composed of the LiCl/MWCNT/PVA obey the exponential equation both for heat storage and heat release stage:

$$q(t) = w(t)/w_{fin} = 1 - exp(-t/\tau) \tag{1}$$

where $w(t)$ – amount of water adsorbed by the composite relating to time t, w_{fin} – final amount of sorbed water relating to equilibrium state. The characteristic time is in the range τ = 90-300 s. It was shown that for heat release stage grains 0.4-0.5 mm demonstrate higher sorption rate than grains 0.8-0.9 mm. During heat storage stage two grain sizes under consideration are characterized by approximately same rate of desorption process. The reason of this fact is probably higher vapour pressure during desorption stage overcoming diffusive difficulties concerning with higher grain size. The data on water sorption dynamics on the loose grains of

LiCl(55)/MWCNT/PVA (Fig. 1) allows the estimation of the Specific Power of SHS unit as $SP_{0.8}=0.8\Delta w_c$ $Q_{is}/(t_s)$, where t_s is the duration of the stage.

Table 2

The Specific Power of SHS unit under conditions of the DS cycle

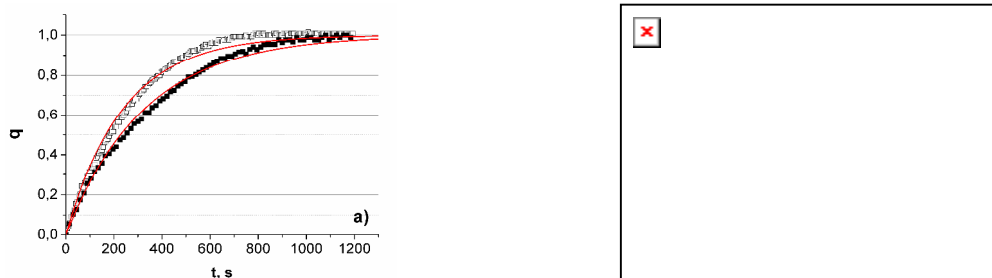| Grain size	$SP_{0.8}$, kW/kg	
	Heat release stage	Heat storage stage
0.8-0.9 mm	4.1	9.7
0.4-0.5 mm	2.9	9.8

Fig. 1. The kinetic curves (symbols) of water sorption/desorption on LiCl(55)/MWCNT/PVA composite and their exponential fitting (lines) under conditions of the DS cycle: (a) sorption P = 0.88 kPa, ΔT = 65-35 ℃ and (b) desorption, P = 1.23 kPa, ΔT = 46-85 ℃. 0.8-0.9 mm - solid symbols and 0.4-0.5 mm - open symbols

The conversion was restricted by q = 0.8 in order to avoid strong falling down of the power at approaching to the equilibrium. For the DS cycle, the SP for discharging and charging stages are in the range of 2.9-4.1 kW/kg and 9.7-9.8 kW/kg respectively. One can see that under conditions of the DS cycle one needs only 0.5-1.5 kg of the new sorbent to realize a 2 kW heating power that is promising.

Conclusion. Owing to high HSC and SP values the new composite LiCl(55)/MWCNT/PVA promises great potential for realization of the DS heat storage cycle.

This work was conducted within the framework of budget project No. AAAA-A17-117041110045-9 for the Boreskov Institute of Catalysis.

REFERENCES
1. Aydin, D., Casey, S. P., Riffat S. (2015). The latest advancements on thermochemical heat storage systems [Electronic version]. Renewable and Sustainable Energy Reviewers, no. 41, pp. 356–367.
2. Yu, N., Wang, R, Z., Wang, L.W. (2013). Sorption thermal storage for solar energy [Electronic version]. Progress in Energy and Combustion Science, no. 39, pp. 489–514.
3. Levitskii, E., Aristov, Y., Tokarev, M., Parmon, V. (1996). "Chemical Heat Accumulators" - a new approach to accumulating low potential heat [Electronic version]. Solar Energy Materials and Solar Cells, no. 44, pp. 219-235.
4. Grekova, A., Gordeeva, L., Aristov, Y. (2016). Composite sorbents "Li/Ca halogenides inside Multi-wall Carbon Nano-tubes" for Thermal Energy Storage [Electronic version]. Solar Energy Materials and Solar Cells, no. 155, pp. 176-183
5. Sapienza, A., Santamaria, S., Frazzica, A., Freni, A., .Aristov Yu. (2014). Dynamic study of adsorbers by a new gravimetric version of the Large Temperature Jump method [Electronic version]. Applied Energy, no. 113, pp.1244-1251.