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ECOS 2023: The Energy Storage Capabilities Of Single And Mixture Sorbent Salts Impregnated Pumice And Anodic Aluminium Oxide Based Composite Materials

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Abstract:

In recent years, when the energy demand has increased day by day, the continuity of energy has become an important issue as well as the need to meet the demand from nature-friendly technologies. Thermochemical Heat Storage (THS) systems are among the important approaches that help the continuous and efficient use of renewable energy resources with its high energy storage density and long storage times. Researches on composite structures consisting of sorbent salt and porous matrix couple among storage materials are noteworthy for the development of sorption materials and thus the heat storage system. Composite sorbents were prepared by impregnating sorbent salt ($CaCl_2$ and $MgCl_2$ etc.) as single and mixture into two different matrix materials, anodic Aluminium oxide (AAO) template and pumice (P), is carried out in this study. The cyclical heat storage behaviours of the obtained composite structures were investigated with the laboratory scale thermochemical heat exchanger prototype system. The aim of this study is that the effect of host matrices with different pore diameters one of whose is produced in the laboratory and other is natural on the thermochemical heat storage capability. Moreover, different sorbent salts which are impregnated into these pores on the heat storage capability is also compared with the help of prototype system.

Keywords:

Thermal Energy Storage (TES), AAO templates, Pumice, Composite Material, Salt-impregnation.

1. Introduction

The visible and tangible negative effects caused by the use of fossil fuels shows that we are facing a global climate crisis. Due to the intermittent nature of renewable energy sources, a great majority of the energy demand today is still met by fossil fuels [1]. While this situation reveals the importance of storage for the efficient use of the energy, it is also critical to improve these systems in order to meet the energy demand of the increasing population with environmentally friendly and sustainable technologies [2,3]. Thermal Energy Storage (TES), one of the energy storage approaches, has important application areas such as the efficient use of intermittent solar energy and the recovery of low-grade industrial waste heat released directly into the atmosphere [4,5]. There are three types of TES systems such as sensible, latent and thermochemical heat storage [3,6]. Thermochemical Heat Storage (THS) systems, in which heat is stored and released as a result of the reversible sorption-desorption process, are remarkable for their long storage times and high energy storage density [7,8]. In sorption heat storage systems, heat is stored as a result of physical changes in the storage medium. During the charging (desorption) process, hot dry air (eg, waste heat, heat emitted from solar collectors) is passed through the storage material to remove absorbed water. As a result of the endothermic reaction, heat is stored by the material as potential energy. During the discharge (sorption) process, water vapour absorption occurs by passing humid air through the storage material and the stored heat is released. As long as the storage material is not in contact with humid air, heat is stored with almost no loss [9,10]. For storage systems with low thermal losses and high energy storage capacity, mass and heat transfer are expected to be high as well as the material maintaining thermal, physical and cyclic stability [8]. Therefore, the development of storage mediums is very important for the improvement of these systems.

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In recent years, composite materials obtained by impregnated sorbent salt into a porous host matrix are among the prominent sorption materials [6,11]. In the literature, many porous matrices with different pore diameters and surface areas are used as a structural support for sorbent salts such as zeolite [12], silica gel [13], activated carbon [14], attapulgite [15], wakkanai siliceous shale (WSS) [4], vermiculite [16], etc. The porous matrix helps to maintain the physical stability of the material during repetitive cycles while also improving mass and heat transfer [17]. In recent studies for the development of sorption materials, in addition to natural rocks, new generation porous materials such as MWCNT [18], MOF [19], AAO [20], silicone foam [21], concrete [22], which are synthesized in the laboratory, are also preferred as host matrix.

Sorbent salts, the main absorbing component that stores heat, are notable for their high energy storage densities [2]. The existence of problems such as deliquescence and agglomeration that make the use of sorbent salts difficult is stabilized by the porous host matrix [23]. In the literature, many sorbent salts such as $CaCl_2$, LiCl, $LiNO_3$, $MgCl_2$, $SrBr_2$, $SrCl_2$, LiBr, $MgSO_4$, K_2CO_3 are used for sorption heat storage with host matrix [2]. Also salt mixtures are impregnated into porous matrices in order to improve their water uptake capacity and operate at relatively low regeneration temperatures [6,15]. Different porous matrix/salt pairs are investigated to develop systems with high energy storage capacity and cyclic stability [24]. Nejhad et al. [22], the cyclic heat storage capacities of the composite sorbents they synthesized with 3 different porous matrices (aerated porous concrete, vermiculite, zeolite) were investigated with a laboratory scale fixed-bed open THS prototype system. Accordingly, energy storage densities of 196-175, 180-163, and 251-114 kWh/m^3 were obtained, respectively, for APC-$CaCl_2$, vermiculite-$CaCl_2$ and zeolite-$CaCl_2$ composites at low regeneration temperature (85-95 °C). Mehrebadi et al. [25] investigated the composite sorbents prepared with two porous (pumice, expanded clay) matrix and different sorbent salts ($Al_2(SO_4)_3$, $MgSO_4$, $CaCl_2$, $MgCl_2$, $SrCl_2$) using a laboratory scale filled bed reactor. According to the results, $SrCl_2$ has the highest energy storage density (29 kWh/m^3 for expanded clay and 7.3 kWh/m^3 for pumice) and the study points out that pumice has cyclic stability. Yilmaz et al. [26], used anodic Aluminium oxide (AAO) templates produced with two step anodization method in the laboratory as porous host matrix for four different sorbent salts and their mixtures. The energy storage densities obtained for AAO-LiCl and AAO-CaCl2 composites as a result of DSC analysis are 242.2 and 220.8 kJ/kg, respectively.

In this study, anodic aluminium oxide (AAO) templates and pumice (P) used as porous host matrix. Composite materials were prepared by impregnating mono and mixed sorbent salts ($CaCl_2$, $MgCl_2$) into host materials. AAO templates with pore size controlled by electrochemical process parameters were produced in the laboratory with a two-step anodization process. The aim of the study is to compare the behavior of sorbent salts impregnated into different host matrices. For this purpose, the cyclical energy storage density (E_d) of the obtained composite materials were investigated with the laboratory scale thermochemical heat exchanger prototype system.

2. Materials and Method

In this study, anodic Aluminium oxide produced by anodization from 99.99% pure aluminium and pumice, a natural rock, were used as host material in order to be able to absorbed sorbent salts. AAO templates were obtained by applying two-step anodization method to high purity (99.99%) aluminium plates. Aluminium plates were immersed in an isopropyl alcohol at 35-40 °C in an ultrasonic bath for 10 minutes prior to anodization and then they etched in an etching solution containing $CuSO_4$, H_3PO_4 and HNO_3 at 85 °C for 2 minutes. Following these processes, two-step anodization process was started. Aluminium plates were anodized in a 0.6 M oxalic acid solution at 10 °C at 40 V for 30 minutes during both the first and second step anodization process. AAO with regular pore structure were obtained at the end of second anodization step. AAO samples obtained via the two-step anodization method were immersed in 0.1 M NaOH solution for 15 minutes in order to enlarge the existing pore diameter prior to salt impregnation. Then the moisture in the pores was evaporated by keeping it in an oven at 110 °C for 24 hours. The similar procedure was also applied to pumice to be completely dehumidified and ready for salt impregnation. The dried AAO and pumice templates were filled with two mono salts and their mixtures.

In order to be able to obtain composite structure, matrix materials (AAO and Pumice) completely were immersed into saturated mono and mixed salts and they were hold at 10 Psi and 30 ^oC under vacuum for 48 h. This aimed to fill existing pores with salt solution via capillary action. Dry sample weights before and after salt impregnation are given in Table 1. The amount of impregnated salt in pumice was measured by taking the sample weight before and after the salt impregnation. The amount of salt absorbed per unit area for AAO samples was calculated empirically by dividing the amounts of salt impregnated into each sample by the total surface area as in our previous study [26].

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Table 1. Dry sample weights before and after salt impregnation.

Impregnated salt and ratios	Sample weight before salt impregnation (g)	Sample weight after salt impregnation (g)
Matrix: AAO		
$CaCl_2$	0.157	0.278
$MgCl_2$	0.149	0.349
$CaCl_2$ + $MgCl_2$ (1:1)	0.133	0.219
Matrix: Pumice		
$CaCl_2$	16.12	42.29
$MgCl_2$	16.24	40.72
$CaCl_2$ + $MgCl_2$ (1:1)	17.01	43.03

2.1. Characterization

Microstructures of both AAO and pumice, acting as a matrix, before and after salt impregnation were investigated with Zeiss brand Sigma 300 model FESEM. Theoretical thermal energy storage capacities of the composites were characterized using a Differential Scanning Calorimetry (DSC). Analyses were performed with a TA Instruments Q2000 model DSC instrument in the temperature range of 30-140 °C, according to BS EN ISO 11357-4 standards. In addition, composite materials were characterized by a laboratory-scale prototype. Figure 1 shows the prototype system consisting of a humidifier, heater, cabinet and fan.

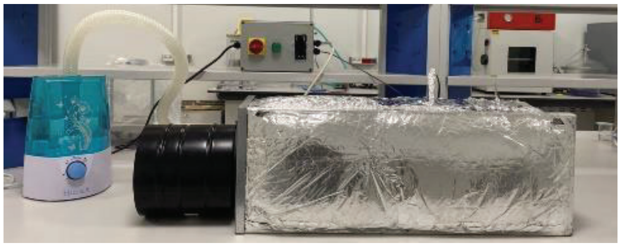

Figure 1. Thermochemical heat exchanger prototype.

In the prototype system, experiments were carried out as three consecutive discharge-charge cycles and the cyclic behaviour of composites were investigated. During discharge process, the air was humidified and blown through the cabin with help of a fan. The humid air was passed through across the composite material. Water vapour was absorbed by the composite and heat released during this time. During charging process, air was heated to 80-85 °C with the help of an electric heater and hot dry air passed across the composite material. Meanwhile, moisture inside the composite was removed and heat stored.

3. Results and Conclusions

In this study, the results show that the average pore diameter of AAO film was about 85±5 nm as shown in Figure 2(a). The pores were regular and high ordered. Figure 2(b) shows a cross-sectional view of the AAO template.

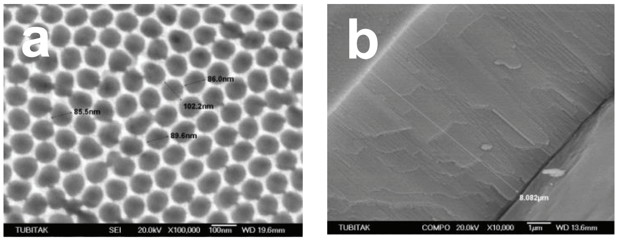

Figure 2. FESEM image from top: a) and cross-section b) of AAO template

The average thickness of the nanotubes is approximately 8μm. The increase of the lengths of the nanotubes depends on the increase of the anodization period. The lengths of the nanotubes are directly proportional to the duration of second step of the two step anodizing. The images of pumice, used as matrix material, before and after salt impregnation are given in figure 3.

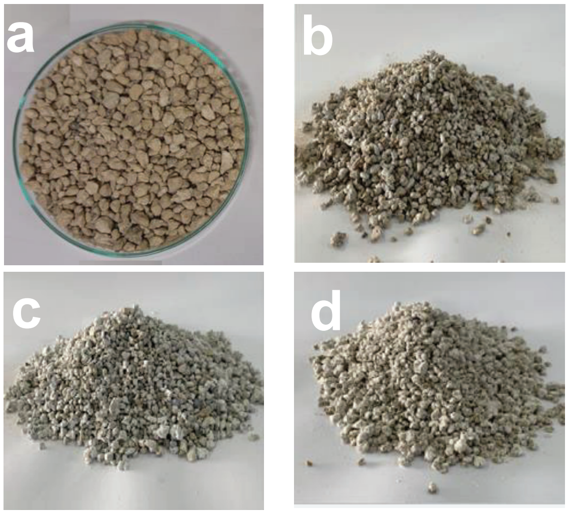

Figure 3. Images of pumice: a) before salt impregnation, b) $CaCl_2$ impregnated, c) $MgCl_2$ impregnated and d) mixed sorbent salts impregnated.

Figure 4 shows the FE-SEM images obtained after salt impregnation of both matrix materials: (a) AAO-based composite structure following salt impregnation, (b) pumice before salt-impregnation, and (c) pumice-based composite structure following salt impregnation. SEM images show that the pores of both matrix materials could be filled with sorbent salts.

Energy storage density (Ed), is one of the important parameters for evaluating the suitability of any material for THS application. In this regard, after synthesizing composites structures of salt impregnated, Ed of these materials were evaluated through characterization methods. For the DSC analysis, synthesized materials were kept in a moist environment (RH=90%) over 48 hours to ensure that they are saturated with water. Later on the fully hydrated materials were placed within DSC device. For evaluating the Ed, total energy consumption for moisture desorption (until the material reaches anhydrous state) was calculated. Within the DSC studies, the specific heat capacity (Cp) is determined with the Equation (1). In the Equation ΔQ and ΔT represents the variation of heat supplied to the material and the variation of the applied desorption temperature with the time, while m shows the mass of the sample by integrating the area under the desorption heat–Cp curve.

$$Cp = \Delta Q/(m.\Delta T) \tag{1}$$

Theoretically, total energy consumption for moisture desorption in charging could be considered equal to the thermal energy generated in discharging process for the same amount of moisture adsorption. Consequently, energy density of the material could be obtained by calculating the ratio of desorption energy consumption to the weight of the sample [26]. As shown Table 2, the highest theoretical Ed value was obtained for $MgCl_2$ impregnated into both pumice and AAO. On the other hand, $CaCl_2$ has also the lowest E_d value for both host matrices.

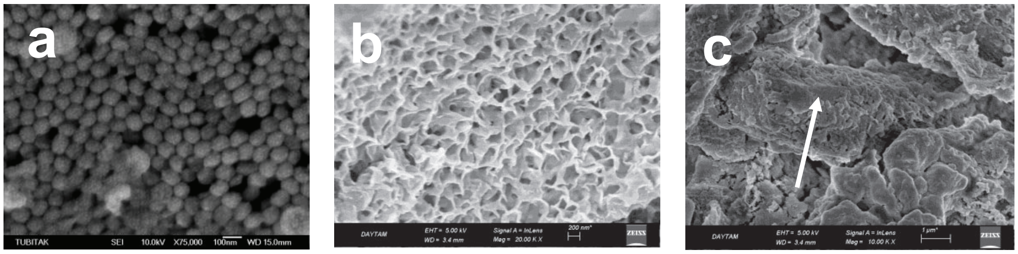

Figure 4. FESEM images of a) AAO after salt impregnation, b) pumice before salt impregnation and c) pumice after salt impregnation

Table 2. E_d values calculated as a result of DSC.

Samples	E_d (kJ/kg)
AAO-$CaCl_2$	161.68
AAO-$MgCl_2$	836.19
AAO-$CaCl_2$+ $MgCl_2$	795.12
P-$CaCl_2$	1255.83
P-$MgCl_2$	1700.39
P-$CaCl_2$+ $MgCl_2$	1657.41

The heat storage capacities of the composite structures, whose theoretical energy storage capabilities were determined with DSC, were also measured with the laboratory scale thermochemical heat exchanger prototype system. The experiments were carried out as three consecutive discharge-charge cycles for each composite and the cyclic heat storage capabilities of the composite sorbents were obtained. Figure 5 (a) and (b) shows the outlet air temperature (T) changes for AAO and pumice composite materials over three discharge cycles, respectively. The input air temperature was measured 18-20°C as it was affected by the fluctuating room temperature during the experiment. Due to the high absorption rate, temperature rise was observed at the beginning of each cycle in all composites.

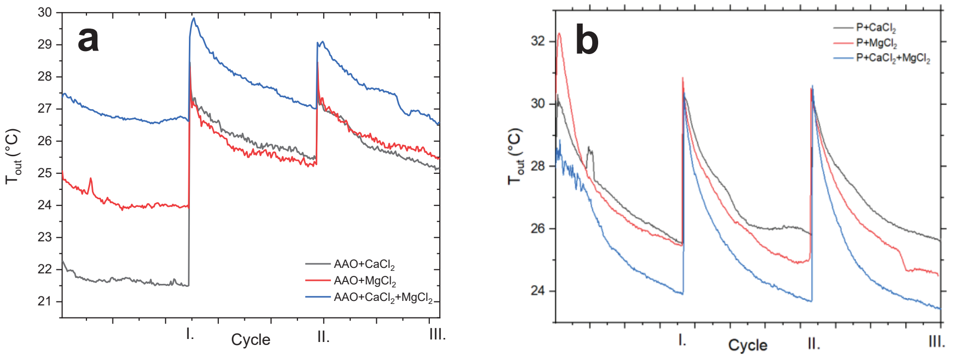

Figure 5. Output temperature changes of (a) AAO matrix composites, (b) pumice matrix composites

The heat output rate (out) values of all composite materials during the discharge process are shown in Figure 6. The heat output rate can be determined based on the enthalpy changes before and after the sorption material (Eq. 2), as well as the mass flow rate (discharge) in the discharge phase, the specific heat (Cp) at constant pressure and the difference between input and output temperatures of the system [22].

$$\dot{Q}_{\text{out}} = \dot{m}_{discharge} C_p (T_{\text{out}} - T_{in}) \qquad (2)$$

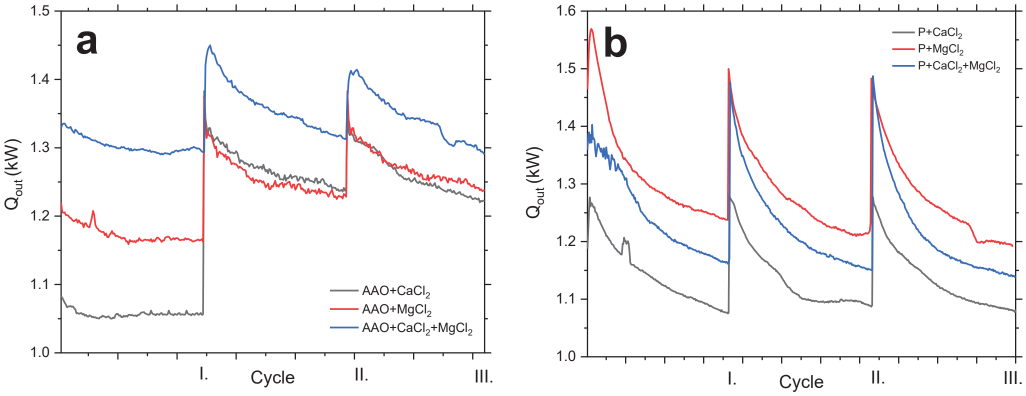

Figure 6. Heat output rate values of six composite materials over three discharge cycles: a) AAO matrix composites and b) pumice matrix composites .

It is seen that the average output heat flow rates for AA0-$MgCl_2$:$CaCl_2$ are 1.29, 1.37 and 1.35 kW for all three cycles, respectively. Just as at the output temperature, the heat flow rates for the mixed salt impregnated sample exhibit also stable behaviour in all three cycles. On the other hand, while the heat flow rate for the AAO-$MgCl_2$ sample is average 1.18 kW in the first cycle, this value reaches the order of 1.28 and 1.29 kW in the second and third cycles, respectively. It is seen that these values for Pumice-$MgCl_2$:$CaCl_2$ are on average 1.25, 1.24 and 1.24 kW. Especially in the first cycle, the sample with the lowest heat flow rate was the AAO-$CaCl_2$ and pumice-$CaCl_2$ samples with 1.06 kW and 1.16 kW, respectively. On the other hand, the reason for the increase in the output heat flow rate of the AAO-$MgCl_2$ and AAO-$CaCl_2$ composites, especially in the 2nd and 3rd cycle, might have been due to the increase of ΔT in the repeated cycles.

The energy storage densities of the system were calculated by the ratio of the total energy output value to the volume of the composite material for the discharge phase to be obtained by integrating the equation (2) over the discharge period [22].The cyclic energy density (Ed) values of the discharge phases of the six composite materials are given in Table 3.

Table 3. *Cyclic energy density (E_d) values of six composite materials over three discharge cycles.*

Matrix	Impregnated salt	Cycle	E_d (kWh/m^3)	Matrix	Impregnated salt	Cycle	E_d (kWh/m^3)
AAO	$CaCl_2$	1	180	Pumice	$CaCl_2$	1	411
		2	92			2	328
		3	70			3	269
	$MgCl_2$	1	131		$MgCl_2$	1	658
		2	99			2	485
		3	88			3	518
	$CaCl_2$ + $MgCl_2$ (1:1)	1	160		$CaCl_2$ + $MgCl_2$ (1:1)	1	597
		2	144			2	469
		3	135			3	418

As can be seen, the highest energy density values were obtained in the mixed salt in AAO matrices and in $MgCl_2$ impregnated samples for pumice matrices throughout all cycles. Accordingly, while the highest energy density value was obtained for the AAO-$MgCl_2$:$CaCl_2$ composite in the first cycle, the highest value was obtained for the pumice-$MgCl_2$ composite in the similar cycle. Ed values of all composite samples obtained using the thermochemical heat exchanger prototype test setup are different from the values calculated as a result of DSC analysis. This result shows that, theoretically, the statement that the total energy absorbed by the material during desorption is equal to the energy it can produce during sorption is not entirely true.

Within this study, mono and mixed salt impregnated AAO and pumice based composite samples were synthesized and characterized for thermochemical heat storage applications. The results obtained are given below:

- In the prototype test setup, the highest Ed value was obtained in the pumice-$MgCl_2$ composite with 658 kWh/m^3.

- As a result of the measurements in the thermochemical heat exchanger prototype, AAO-$MgCl_2$:$CaCl_2$ composite had a high exit temperature in all three cycles and exhibited a high stable performance during repeated cycles compared to AAO-$CaCl_2$ and AAO-$MgCl_2$.

- Similar stable behaviour for all three cycles was also obtained in pumice-$MgCl_2$ composite.

- The fact that the Ed values obtained for AAO-$MgCl_2$:$CaCl_2$ in every three cycles are close to each other, unlike the AAO-$CaCl_{l2}$ and AAO-$MgCl_2$ composites, is an indication that the AAO-$MgCl_2$:$CaCl_2$ composite has cyclic stability, and this is promising for the efficient use of THS systems. Similarly, pumice-$MgCl_2$ is preferable in the efficient use of THS systems.

Acknowledgments

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