Article

Development and Characterization of Composite Desiccant Impregnated with LiCl for Thermoelectric Dehumidifier (TED)

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Abstract: Aqueous salt solutions (LiCl) were impregnated into a porous host matrix to create composite desiccant materials (silica gel). The authors of this paper fabricated and analyzed composite desiccant-coated aluminum sheets (DCAS) with varying LiCl mass concentrations. Nitrogen sorption results revealed that the Brunauer–Emmett–Teller (BET) surface area and pore volume of the composite desiccant-coated aluminum sheets decreased. Furthermore, composite DCAS had lower nitrogen sorption than silica-gel-coated aluminum sheets (SGCAS). According to the results, the composite DCAS had the highest thermal conductivity, measuring $6.1 \text{ Wm}^{-1} \text{ K}^{-1}$, doubling that of the SGCAS. For evaluating sorption kinetics, the linear driving force model (LDF) was used, and composite DCAS showed greater dynamic sorption quantities and sorption rate coefficients than SGCAS. Furthermore, three different moisture sorption isotherm models were used to fit the experimental results: the Brunauer–Emmett–Teller (BET) model, the Guggenheim–Anderson–Boer (GAB) model, and the double log polynomial (DLP) model. The DLP model was shown to be the best model for predicting the moisture sorption isotherms of DCAS. Additionally, the composite desiccant-coated heat sink (DCHS) of the thermoelectric dehumidifier (TED) was evaluated and compared to silica gel in terms of dehumidification capacity. According to the findings, the outlet air humidity ratio of the composite DCHS reached a minimum of 10.23 g kg^{-1} , and the dehumidification capacity was 0.117 kg h^{-1} when the input electrical voltage was kept at 9 V.

Keywords: composite desiccant; sorption kinetic; sorption isotherm; dehumidification capacity; thermoelectric dehumidifier

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1. Introduction

Recognizing the gravity of the problems caused by CO₂ emissions and global warming in recent years, there has been an increase in research efforts aimed at developing solid dehumidification systems powered by low-temperature energy derived from various sources. As a promising energy-saving technology, these systems use massive amounts of industrial waste heat and low-grade solar energy. Instead of CFCs, HCFCs, or HFCs, the systems employ solid desiccant cooling in the form of silica gel. Furthermore, they do not contribute to ozone layer depletion and effectively reduce global warming potential. To improve the overall performance of the systems, the desiccant should typically be capable of high-water adsorption at a specified adsorption temperature while also being readily regenerable at a low regeneration temperature. Silica gels are widely used in solid dehumidification systems due to their high porosity and stable sorption properties. They can be regenerated at low temperatures and are readily available [1]. However, their adsorption capacity is only about 40% of their weight, and water exchange is low during a typical dehumidification cycle because water sorption occurs almost entirely at extremely high pressures, as opposed to lower pressures [2]. To address this issue,

researchers have focused on developing a new desiccant with high adsorption capacity that can be regenerated at low temperatures.

In a previous study, a new family of composite desiccants known as novel composites salt inside porous matrix (CSPMs) was introduced for dehumidification systems, which are two-phase systems composed of a porous host matrix (silica gels, activated alumina, porous carbons, zeolite, and expanded vermiculite, etc.) and aqueous salt solutions (LiCl [3], CaCl₂ [4], LiBr [5], MgCl₂ [6], MgSO₄, Ca (NO₃)₂ [7], Na₂S, SrBr₂, and LiNO₃ [8], etc.). The materials' physical structure places them in a middle ground between solid desiccants and hygroscopic salts, and they were arranged to exhibit the best properties of both materials. Using a composite desiccant (silica gel–haloids) developed by Ge et al. [9], a rotary wheel dehumidification system with an inter-cooling rotary wheel was utilized to remove part of the adsorption heat. The study discovered that the system could be operated at low regeneration temperatures (60 to 90 °C) while maintaining a COP coefficient greater than 1.0. Additionally, using previously validated simulation models, Jeong et al. [10] investigated the performance of four dehumidification systems. In the experiments, a batch-type dehumidification system with an internal heat exchanger was found to operate effectively at heated air temperatures as low as approximately 33 °C. Hu et al. [11] evaluated the performance of fin-tube heat exchangers coated with silica gel and silica gel–lithium chloride (LiCl) composite desiccant. When tested under the same experimental conditions as silica gel, the composite desiccant had an excellent dehumidification capability. Chua [12] investigated the effectiveness of three different types of composite desiccants: silica gel–calcium chloride (CaCl), silica gel–lithium chloride (LiCl), and silica gel–polyvinyl alcohol (PVOH). Composite materials contain a higher percentage of silica gel and halides or polymers, which have strong moisture removal properties when compared to traditional desiccant materials. The high regeneration capacity results showed that composite desiccants outperformed pure silica gel by at least 11% in terms of moisture removal capacity, regeneration rates, and pressure decreases.

Despite this, only a few studies on composite, desiccant-coated aluminum sheets (DCAS) have been published in the literature. Hu et al. [13] developed a composite desiccant-coated aluminum foil using silica gel in various particle sizes and impregnated them with saturated solutions of lithium chloride (LiCl) and calcium chloride (CaCl₂). The composite desiccant increased moisture uptake by more than 30 to 45%, and the LiCl composite desiccant had higher moisture uptake than the calcium chloride composite desiccant. In comparison, the composite desiccant outperformed silica gel by 70 to 120% in terms of cycle adsorption. Zheng et al. [14] investigated how different silica gel–lithium chloride (LiCl) composite DCAS influence the behavior of desiccants. The silica gel–LiCl composite DCAS had twice the maximum thermal conductivity of the silica-gel-coated aluminum sheets (SGCAS), as well as significantly higher dynamic sorption quantities and a higher sorption rate in sorption kinetics. A silica gel–LiCl composite desiccant-coated heat exchanger (DCHE) was compared to a silica-gel-coated heat exchanger in terms of dehumidification capacity. The results demonstrated that, by incorporating a silica gel–LiCl composite desiccant into the DCHE system, it is possible to achieve increased dehumidification capacity.

In this study, composite DCAS with varying LiCl mass concentrations were created and analyzed. This can certainly provide an in-depth understanding of the reaction mechanism during the adsorption/desorption operations on LiCl concentration, thus, leading to valuable information for the advancement of composite desiccant materials. This composite desiccant material was used to coat heat sinks of TED as a method of decreasing the heat load on conventional, vapor-compression refrigeration systems. The texture properties, as well as the microstructure properties, were studied. To determine and analyze sorption kinetics, the linear driving force (LDF) model was used. Moreover, the thermal conductivity was measured and discussed. To fit the experimental data, three moisture sorption isotherm models were used: the Brunauer–Emmett–Teller (BET) model, the Guggenheim–Anderson–Boer (GAB) model, and the double log polynomial (DLP) model.

Finally, the thermoelectric dehumidifier (TED) was used to assess the dehumidification capacity of silica gel and composite DCAS. The advantages of a TED with a desiccant-coated heat sink (DCHS) include the ability to exchange both sensible heat (fin heat sinks) and latent heat (desiccant material) [15,16]. Furthermore, the TED can regenerate the desiccant using the thermoelectric module (hot-side) and reduce the air temperature before entering the room using the thermoelectric module (cold-side).

2. Materials and Methods

2.1. Preparation of Composite DCAS

Table 1 presents the specifications of the materials that were utilized in this study. It was based on the coating technique developed by Zheng et al. [14]. The commercial silica gel was dried at 100 °C for 4 h prior to preparing the composite DCAS. An aluminum sheet was weighed and brushed with liquid glue, followed by the scattering of silica gels onto the glue-adhered sheet. After dipping the aluminum sheet in silica sol for approximately 30 min to thoroughly combine the silica gel, it was dried at 100 °C for 4 h. The aluminum sheets were dipped in silica sol and dried 5 more times. The aluminum sheets were then immersed in an aqueous lithium chloride (LiCl) solution containing various mass concentrations (30, 35, 40, and 45 wt.%) for 12 h before being dried in an oven at 100 °C for at least 6 h until the weight remained constant. The salt content of the composite DCAS was measured by weighing the aluminum sheets before and after salt impregnation.

Table 1. Material specifications for preparing the DCAS.

Name	Description	Manufacturer
Aluminum sheet	60 mm × 40 mm × 1 mm $k = 230 \text{ Wm}^{-1} \text{ K}^{-1}$	AIC Aluminum Profile Service Center (Bangkok, Thailand)
Silica gel	Mesoporous, the grain size of 70 to 230 mesh $S_{\text{BET}} = 500 \text{ m}^2 \text{ g}^{-1}$; $V_t = 0.75 \text{ cm}^3 \text{ g}^{-1}$; $d_{\text{av}} = 6 \text{ nm}$ $k = 0.1 \text{ Wm}^{-1} \text{ K}^{-1}$	Merck PTE Ltd. (Singapore)
Silica sol	30 wt.% suspension in H_2O , $\text{pH} = 9.1$ $S_{\text{BET}} = 230 \text{ m}^2 \text{ g}^{-1}$; $V_t = 0.21 \text{ cm}^3 \text{ g}^{-1}$; $d_{\text{av}} = 4.3 \text{ nm}$	Merck PTE Ltd. (Singapore)
Liquid glue	Polyurethane base (BT550) $k = 0.26 \text{ Wm}^{-1} \text{ K}^{-1}$	Bond Chemicals Co., Ltd.
Anhydrous LiCl	ACS reagent, assay $\geq 99\%$	Merck PTE Ltd. (Singapore) (Bangkok, Thailand)

Table 2 shows the results of this research, which included the fabrication of four composite DCAS. The composite DCAS were labeled SG-L30, SG-L35, SG-40, and SG-L45, where the digital numbers represent the mass concentrations of the impregnating LiCl in the composite DCAS, respectively. The salt content of composite DCAS increased as the impregnating concentration of LiCl solution increased. SGCAS (SG-L0) was also produced as a contrast sample.

Table 2. Experimental parameters of the DCAS.

Composition	Impregnating Concentration of LiCl (wt.%)	Mass of Desiccants (g)	Total Mass (g)	Salt Content (wt.%)	Coating Amount (kg m^{-2})
SG-L0	0	1.05	7.45	0.00	0.44
SG-L30	30	1.18	7.58	12.38	0.49
SG-L35	35	1.20	7.60	14.29	0.50
SG-L40	40	1.23	7.63	17.14	0.51
SG-L45	45	1.27	7.67	20.95	0.53

2.2. Thermal Conductivity

The hot disk thermal constant analyzer (TCA), Hot Disk AB: TPS2500S, was used to measure the thermal conductivity of the DCAS. Thermal conductivity was measured using the standardized transient plane source (TPS) technique, which has an accuracy greater than 5%. The samples were 50 mm × 50 mm × 10 mm in size. Before the test, all of the DCAS samples were oven-dried for 4 h at 100 °C.

2.3. Characterization Techniques

The BET surface area, pore volume, and pore size were measured and analyzed using a surface area and porosity analyzer (Micromeritics-TriStar II 3020, Micromeritics instrument corporation, Norcross, GA, USA). To obtain nitrogen sorption isotherms at 77 K, the system employed the physical adsorption and capillary condensation principles. Temperature and pressure were the main causes of experimental errors. The temperature accuracy of the manifold was ±0.25 °C, and the pressured ones had a testing error of around 0.5%. To determine the morphology of DCAS, scanning electron microscopy (SEM) analysis was performed using a LEO1455VP scanning electron microscope.

2.4. Sorption Kinetics

The kinetics of the DCAS sorption were studied in a constant temperature and humidity chamber. The humidity control range was 10 to 98%, while the temperature range was −70 to 180 °C. The defined working conditions were set at 20 °C and 70% RH. During the test, the temperature fluctuated in the chamber by 0.1 to 0.2 °C while the relative humidity fluctuated by ±2.5%. Before the test, the DCAS samples were dried at 100 °C for 4 h in an oven and weighed. The DCAS were then placed in a chamber with pre-set conditions. The weights of the DCAS were recorded at prescribed times on an electronic scale with an accuracy of 0.001 g, which was used in this study.

2.5. Moisture Sorption Isotherms

The DCAS moisture sorption isotherms were generated using a vapor sorption analyzer (VSA) at 25 °C. The VSA generated dynamic isotherms by employing the dynamic dewpoint isotherm (DDI) method, water activity, and a gravimetric analysis method that does not control water content or activity but dries or wets the sample to measure water activity and water content during the wetting or drying process. A high-precision magnetic force balance was used to weigh the samples to determine water content. Table 3 shows the specifications of the VSA.

Table 3. Vapor sorption analyzer (VSA) specifications.

Physical Parameter	Range or Deviation
Water activity, A_w	0.03–0.95 A_w
Water activity, A_w accuracy	±0.005 A_w (for volatiles setting ± 0.02 A_w)
Sample temperature control range (°C)	15–60 at STP
Operating environment (°C)	4–50
Sample weight (mg)	500–5000
Mass resolution (mg)	±0.5

Vapor sorption analyzer (operator's manual).

2.6. Moisture Sorption Isotherms Models

Moisture sorption isotherms depict the relationship between water activity and moisture content at a constant temperature. It depends on the chemical composition, physical structure, and physical-chemical condition of the material. Due to variations in capillary, surface, and colligative processes, the isotherm shape is unique to each material type. Over the decades, several renowned adsorption models were developed based on monolayer

and multilayer adsorption theories, with the BET [17] and GAB [18] being the most widely used. The BET model is often used to estimate moisture sorption data ranging from 0 to 0.5 A_w [19]. In comparison, the GAB model enhances the BET model's applicability over a broader range (0.05 to 0.95 A_w) [18]. The DLP model [20] is a new empirical model that is even more effective than the GAB model in characterizing complicated isotherms. The ability of the three moisture sorption isotherm models to fit the experimental data for the DCAS was evaluated in this study (BET, GAB, and DLP). The following are the equations for the models:

$$\text{BET} \quad m = \frac{cm_0 A_w}{(1-A_w)(1+(c-1)A_w)} \quad (1)$$

$$\text{GAB} \quad m = \frac{c_1 K m_0 A_w}{(1-K A_w)(1-K A_w + c_1 K A_w)} \quad (2)$$

$$\text{DLP} \quad m = b_3 x^3 + b_2 x^2 + b_1 x + b_0 \quad (3)$$

where m is moisture content (%) and, for Equations (1) and (2), c is a constant related to water binding energy to the primary binding sites, m_0 is the monolayer moisture content (%), A_w is the water activity, c_1 is a dimensionless measure of the strength of water binding to the primary binding sites, and K is a constant related to the adsorption energies of multilayer adsorption sites. In the GAB model, which differs from the BET theory, the difference in adsorption energies between monolayer and multilayer adsorption sites is represented by an additional adsorption parameter (K). The GAB model may be reduced to the BET equation when parameter $K = 1$. Moreover, in Equation (3), $x = \ln(-\ln(A_w))$; b_0 , b_1 , b_2 , and b_3 are empirical constants. The BET, GAB, and DLP models were fitted using non-linear regression. The Origin 9.0 software was used to perform regression calculations. In addition to the coefficient of determination (R^2) of the non-linear regression, the goodness of the model fit was tested using the root mean square error (RMSE).

3. Results

3.1. Thermal Conductivity

The thermal conductivity for the DCAS is presented in Figure 1. In the result, the thermal conductivity of the DCAS varied from 3.0 to 6.1 $\text{Wm}^{-1} \text{K}^{-1}$, with all DCAS exhibiting good thermal conductivity due to the advantage of the aluminum sheet. Furthermore, the salt content of composite DCAS influenced thermal conductivity significantly. Compared to SGCAS (SG-L0), thermal conductivity increased by impregnating aluminum sheets with salt particles. Due to the immersed salt particles filling some pore space inside the silica, the highest thermal conductivity of composite DCAS (SG-L45) was approximately twice that of SGCAS (SG-L0) [14,21].

Figure 1. Thermal conductivity of the DCAS.

3.2. Textural and Morphological Characterization

Table 4 shows the textural characteristics, including BET surface area (S_{BET}), pore volume (V_t), and average pore size (d_{av}) of DCAS. The calculated parameters were based on the unit mass. S_{BET} and V_t decreased as the mass concentration of LiCl solution in the impregnating solution increased. However, S_{BET}^* and V_t^* were slightly reduced when salt content was considered. Salt surface complexes were formed as a result of various interactions between silica gel and LiCl during impregnation [22]. A similar phenomenon was observed by a number of other researchers [7,23–26]. Furthermore, the d_{av} of composite DCAS decreased slightly due to the complex nature of the LiCl that formed on the silica surface during deposition. The formation of the LiCl layer completely or partially filled the small holes [7,22]. Consequently, d_{av} increased, decreased, or remained relatively constant. Figure 2 depicts the nitrogen sorption isotherms of the DCAS (SG-L0 to SG-L40), with silica gel as a comparison sample. The DCAS exhibited typical type IV isotherms at relative pressures ranging from 0.45 to 0.8, with a hysteresis loop at high relative pressure, according to the IUPAC classification [27]. Type IV isotherms are commonly seen in mesoporous materials (with pores ranging in size from 2 to 50 nm) and indicate multilayer adsorption followed by capillary condensation [28]. Furthermore, the shape of the pores in the studied material was determined by the type of hysteresis. The hysteresis loops for DCAS were of type H1, indicating agglomerates or spherical particles arranged fairly uniformly, as well as relatively high pore size uniformity and facile pore connectivity [29,30]. Furthermore, the capillary condensation process caused a rapid rise in nitrogen sorption at the beginning of the hysteresis loop. Moreover, at a relative pressure of about 1.0, the composite DCAS had a lower nitrogen sorption quantity than SGCAS (SG-L0), because the immersed salt particles blocked some of the silica gel's narrow pores [31]. To further understand the pore structure in DCAS, pore size distributions were also analyzed, as shown in Figure 3. The DCAS showed a sharp peak in the mesoporous region at approximately 4 nm. However, because the immersed salt particles caused pore blockage, the amount of nitrogen sorption by the composite DCAS was significantly reduced.

Table 4. Texture characteristics of the composite DCAS.

Composition	Impregnating Concentration of LiCl (wt.%)	Salt Content (wt.%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{BET}^* ($\text{m}^2 \text{g}^{-1}$)	V_t ($\text{cm}^3 \text{g}^{-1}$)	V_t^* ($\text{cm}^3 \text{g}^{-1}$)	d_{av} (nm)
SG-L0	0	0.00	208.10	-	0.31	-	3.71
SG-L30	30	12.38	128.55	154.31	0.21	0.25	3.74
SG-L35	35	14.29	117.33	147.07	0.18	0.22	3.86
SG-L40	40	17.14	89.59	125.26	0.14	0.19	3.69
SG-L45	45	20.95	59.49	103.09	0.10	0.16	3.68

* Salt content in DCAS was considered.

Figure 4 shows scanning electron microscopy (SEM) images of the DCAS. When viewing the images from Figure 4b–f, it is clear that, as the mass fraction of LiCl increased, the LiCl gradually occupied the microporosity of the silica pellet. It was demonstrated, however, that all composite DCAS had a salt layer that partially covers their matrix surface. LiCl was not entirely contained within the pores and was partially deposited on the outside surface of the grain. Furthermore, the SEM images show potential explanations for the thermal conductivity trend in Figure 1 and the nitrogen sorption isotherm trend in Figure 2. Thermal conductivity initially increased with increasing LiCl concentrations for composite DCAS with the same silica gel ratio because composite DCAS had a more organized structure. Similarly, a higher LiCl concentration during the gas transfer decreased nitrogen adsorption because the silica gel may have been overly squeezed, leaving fewer empty spaces for gas passage.

Figure 2. Nitrogen sorption isotherms of silica gel and DCAS.

Figure 3. Pore size distributions of silica gel and DCAS.

Figure 4. The scanning electron microscopy (SEM) image of (a) silica gel, (b) SG-L0, (c) SG-L30, (d) SG-L35, (e) SG-L40, and (f) SG-L45.

3.3. Sorption Kinetics

The water sorption kinetics of solid desiccant systems are essential since they can influence the cycle time. Experimental results are illustrated in Figure 5. During the initial stages of sorption, dynamic water sorption increased significantly for all DCAS. After that, as the amount of absorbed water approached saturation, it gradually increased. In compar-

ison to SGCAS (SG-L0), composite DCAS demonstrated greater water sorption quantities and rates, indicating a collaborative contribution of the porous host matrix (silica gel) and impregnated salt particles (LiCl). The water sorption quantities of composite DCAS (SG-L40), after testing at 10, 30, and 60 min, were 0.22, 0.30, and 0.34 g g⁻¹, whereas the water sorption quantities of SGCAS (SG-L0) were 0.04, 0.09, and 0.12 g g⁻¹, respectively. This is due to the fact that water sorption through silica gel is a physical process, as opposed to through composite desiccants, which includes both chemical (salt hydration) and physical sorption [14]. Furthermore, because the composite DCAS had higher thermal conductivity than the SGCAS, the influence of the released sorption heat decreased, resulting in a shorter time required to reach sorption equilibrium. When the sorption time exceeded 20 min, the water sorption quantities increased significantly as the LiCl concentrations of the composite DCAS increased.

Figure 5. Water adsorption kinetics curves of DCAS.

Furthermore, sorption rate coefficients were investigated to better understand the dynamic properties of DCAS. As seen in Figure 5, the dynamic sorption curves were approaching exponential. It was possible to use the LDF model to determine the adsorption rate [32]. The sorption rate can, therefore, be represented by:

$$\frac{dx}{dt} = k(x - x_t) \quad (4)$$

where dx/dt is the sorption rate, k is the sorption rate coefficient, (s⁻¹), x is the equilibrium water sorption quantity (g g⁻¹), and x_t is the dynamic water sorption quantity (g g⁻¹).

After the integration of Equation (4), the dynamic water sorption quantity of DCAS can be calculated:

$$x_t = x(1 - \exp(-kt)) \quad (5)$$

Rearranging Equation (5) and using the Napierian logarithm results in the following:

$$-\ln\left(1 - \frac{x_t}{x}\right) = kt \quad (6)$$

The sorption rate coefficients (k) and coefficient of determination (R^2) of SGCAS (SG-L0) and composite DCAS (SG-L30 to SG-L45) were calculated, as shown in Figure 6.

The sorption rate coefficients (k) of the DCAS ranged from 0.77×10^{-3} to $1.78 \times 10^{-3} \text{ s}^{-1}$, which is approximately 1 time greater than SGCAS, indicating the positive effect of LiCl. The LDF model corresponded with well-measured data, with the coefficient of determination (R^2) ranging between 0.983 and 0.996 for all DCAS. When compared to SGCAS (SG-L0), the dynamic water sorption quantity and sorption rate coefficient significantly increased.

Figure 6. Sorption rate coefficients of DCAS.

3.4. Moisture Sorption Isotherms

As shown in Figure 7, the VSA was used to study delicate moisture sorption isotherms on DCAS to better understand the mechanism of moisture sorption behavior of DCAS. The moisture content (%) of composite DCAS (SG-L40) was significantly higher than that of SGCAS (SG-L0) because of the highly hygroscopic salt LiCl contribution. However, moisture sorption isotherms indicated that composite DCAS (SG-L40) had a higher adsorption capacity, with a 20 to 30% greater water uptake than SGCAS (SG-L0). For DCAS, moisture content (%) increased as water activity (A_w) increased.

Figure 7. Moisture sorption isotherms of DCAS.

3.5. Moisture Sorption Isotherms Models

Table 5 shows that, regardless of sorption direction, the DLP model is the best fit for estimating the moisture sorption isotherms of DCAS (R^2 and RMSE), followed by the GAB and BET models. As expected, the BET model fitted sorption data quite well, but only in the water activity (A_w) range of 0 to 0.5. Only the GAB and BET models provided values for monolayer moisture content (m_0), which represent the adsorption potential and amount of water adsorbed to DCAS pore surface monolayer sites for each sorption direction. The higher m_0 values for composite DCAS (SG-L40) showed that this LiCl had a significant effect on sorption behavior, indicating that monolayer moisture content increased with increasing LiCl mass concentrations. Similarly, in the GAB model, the K value increased as the strength of the interactions between the water molecules and the adsorbent increased, compensating for differences in the characteristics of the multilayer molecules compared to the bulk liquid [21].

Table 5. Estimated parameters of models for the moisture sorption isotherms of DCAS.

Model	Para.	SG-L0		SG-L40	
		Adsorption	Desorption	Adsorption	Desorption
BET	c	3.33187	16.1423	2.62282	8.41901
	m_0	0.35426	0.40358	0.43488	0.49152
	R^2	0.91465	0.70074	0.92648	0.75911
	RMSE	0.2570	0.47098	0.26471	0.56232
GAB	c_1	1.60935	1.13943	1.46069	0.9858
	K	0.94432	0.70814	0.96112	0.7583
	m_0	0.50833	1.61023	0.56778	1.78218
	R^2	0.9516	0.93344	0.95263	0.93973
	RMSE	0.19354	0.22213	0.21248	0.28126
DLP	b_0	0.36629	0.78821	0.40107	1.15945
	b_1	−2.49502	−7.17614	−1.05856	−10.01023
	b_2	5.24140	21.08981	−0.49086	26.20371
	b_3	−2.49502	−12.18092	6.04448	−13.72783
	R^2	0.99198	0.98990	0.99255	0.98878
	RMSE	0.07878	0.08651	0.08428	0.12138

On the other hand, when the mass concentration of LiCl was increased, the interactions between surface groups and water molecules decreased, resulting in reduced c and c_1 value. Several layers of water molecules were arranged around each hydrophilic site during the formation of hydration monolayers. The sorption energy decreased as the distance between water molecules and the sorption site increased during the second hydration phase due to the progressive saturation of hydrophilic sites [33]. The direction of sorption is explained by the DLP-fitting equation as given in Table 6, and it was possible to determine the moisture content (%) of DCAS with known initial water activity more quickly.

Table 6. Best fit equations for DCAS experimental moisture sorption data.

Composition	Sorption Direction	DLP Fitting Equations
SG-L0	Adsorption	$m = 0.44693x^3 + 5.2414x^2 - 2.49502x + 0.36629$
	Desorption	$m = -12.18092x^3 + 21.08981x^2 - 7.17614x + 0.78821$
SG-L40	Adsorption	$m = 6.04448x^3 - 0.49086x^2 - 1.05856x + 0.40107$
	Desorption	$m = -13.72783x^3 + 26.20371x^2 - 10.01023x + 1.15945$

m is the moisture content (%), and x is the water activity (A_W).

3.6. Dehumidification Performance

To investigate the application of composite desiccants further, a TED with a composite (SG-L40-DCHS) and silica gel (SG-L0-DCHS)-coated heat sink was built with a desiccant thickness of 1.5 mm. A schematic of the structure of the TED is illustrated in Figure 8a. The TED comprised twelve thermoelectric (TE) cooling modules (TEC1-12708) sandwiched between four aluminum, rectangular heat sinks (two for hot and two for cold air), as shown in Figure 8b. The TE modules were connected in series and arranged in two rows, each containing six TE modules. A total of four direct-current (DC) blowers were employed: two for the hot side, which were primarily used to assist in transferring excess heat to the environment, and two for the cold side, which were used to improve the convection of the air moving through the fin heat sink on the cool side. During the experiment, an electrical voltage was supplied to the TE modules at different voltages of 3, 6, 9, and 12 V, respectively. The cycle time was set at 60 min. The humidity ratio and velocity of the input air were 13.19 g kg^{-1} and 1.2 m s^{-1} , respectively.

Figure 8. Schematic of (a) thermoelectric dehumidifiers (TED) and (b) the air-to-air TED system.

The dehumidification system comprised two dehumidifier units. One of the dehumidifier units worked on the dehumidification process, so it was supplied with the cold side of the TE modules to adsorb moisture in ambient air, whereas the other worked on the regeneration process, so it was supplied with the hot side of the TE modules to remove water from the saturated desiccant. These two dehumidifiers worked simultaneously; while one dehumidified the working air, the other was regenerated. The two switched their operations periodically to achieve dehumidification of the work in process.

Figure 9 shows the effect of increasing the electrical voltage on the cold and hot sides of the thermoelectric module. For the tests, four different voltages were used: 3, 6, 9, and 12 V. The cold-side temperature decreased from 45 to 19 °C as the electrical voltage increased. Meanwhile, when the electrical voltage increased, the temperature on the hot side increased. The maximum temperature on the hot side was 45 °C at 12 V. The minimum temperature on

the cold side was 19 °C at 9 V. The higher the electrical voltage, the lower the temperature on the cold side and the higher the temperature on the hot side. Figure 10 compares the dehumidifying processes under different input electrical voltages of the thermoelectric module. It can be seen that the outlet air humidity ratio depended strongly on the input electrical voltage of the thermoelectric module. In this experiment, when the input electrical voltage was 3, 6, and 9 V, the outlet air humidity ratio (Figure 10a) reached 12.40, 12.34, and 12.26 g kg⁻¹ for SG-L0-DCHS and 11.62, 11.46, and 10.23 g kg⁻¹ for SG-L40-DCHS. In contrast, for the input electrical voltage of 12 V, the outlet air humidity ratio showed an increasing tendency. The outlet air humidity ratio was 11.53 g kg⁻¹ for SG-L0-DCHS and 10.43 g kg⁻¹ for SG-L40-DCHS, respectively. As a result, the outlet air temperature tended to be the same as the humidity ratio (Figure 10b).

Figure 9. Hot- and cold-side temperatures of thermoelectric module versus electrical voltage (hot-side air flow rate: 0.034 m³ s⁻¹, cold-side air flow rate: 0.017 m³ s⁻¹).

Figure 10. The outlet air (a) humidity ratio and (b) temperature under different electrical voltages to thermoelectric module (hot-side air flow rate: 0.034 m³ s⁻¹, cold-side air flow rate: 0.017 m³ s⁻¹).

This result is explicable by the material properties of thermoelectric modules. The heat absorbed from the ambient by a thermoelectric module came from two sources: one due to the Peltier effect, which is proportional to the module's current, another the Joule effect, which is proportional to the square of the current passing through the module. When the input voltage was too low, the Peltier effect was ineffective, resulting in a slow rate of dehumidification. On the other hand, when the input voltage was excessive, the Joule effect took over, imposing a large heat load on the heat-cold heat sinks. Once the generated heat could not be dissipated into the ambient, it was transferred to the cold side via heat conduction, thereby weakening the condensing heat transfer on the fin heat sink.

Dehumidification capacity (Q_{de}) was one of the most critical performance indicators in the DCHS system and was calculated using the following equation [14]:

$$Q_{de} = m_a \left(\int_0^{t_{de}} (w_{ai} - w_{ao}) dt \right) / t_{de} \quad (7)$$

where Q_{de} is dehumidification capacity (kg h^{-1}), m_a is the mass flow rate of process air (kg s^{-1}), w_{ai} and w_{ao} are humidity ratios of process air at the inlet and outlet (g kg^{-1}), and t_{de} is dehumidification time (s). Figure 11 shows the Q_{de} of the DCHS using the TED. With increasing electrical voltage to the thermoelectric module, the Q_{de} increased from 0.031 kg h^{-1} at 3 V to 0.034 kg h^{-1} at 6 V and then reached the maximum value of 0.076 kg h^{-1} at 9 V. A further increase of electrical voltage to 12 V resulted in a slight decrease in the Q_{de} from 0.076 to 0.066 kg h^{-1} for SG-L0-DCHS. Similarly, the Q_{de} of SG-L40-DCHS, after testing at 3, 6, 9, and 12 V, was 0.062 , 0.069 , 0.117 , and 0.110 kg h^{-1} , respectively. Additionally, SG-L40-DCHS removed more moisture from the process air, which was approximately 1 time greater than SG-L0-DCHS. This was due to the combined effect of silica gel with impregnated LiCl.

Figure 11. Dehumidification capacities of DCAS under different electrical voltages to thermoelectric module.

4. Conclusions

The maximum thermal conductivity of composite DCAS was $6.1 \text{ W m}^{-1} \text{ K}^{-1}$, which was more than double that of the SGCAS. Thermal conductivity analysis showed that all of the DCAS examined had good thermal conductivity. The average pore size of composite DCAS decreased slightly due to the complex nature of the LiCl that formed during the deposit on the silica surface. The dynamic sorption quantities and sorption rate coefficients of composite DCAS were greater than those of SGCAS. Composite DCAS had sorption rate coefficients that were approximately 1 time greater than SGCAS. This is because immersed LiCl particles blocked some of the silica's narrow pores. The SEM image shows that, as the mass fraction of LiCl increased, the LiCl salt gradually occupied the microporosity of the silica pellet and was partially deposited on the grain's external surface. Moisture sorption isotherms showed that composite DCAS had a higher adsorption capacity than SGCAS, with a 20 to 30% higher water uptake. The outlet air humidity ratio of the DCHS reached a minimum of 10.23 g kg^{-1} , and the dehumidification capacity was 0.117 kg h^{-1} when the input electrical voltage was kept at 9 V. Furthermore, SG-L40-DCHS removed more moisture from the process air, which was approximately 1 time greater than SG-L0-DCHS. Additionally, the desiccant coating prevented liquid drops from condensing on the cold-side fins. Eliminating condensed liquid drops effectively is a significant future work.

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Nomenclature

A_w	Water activity
b_0	Empirical constant
b_1	Empirical constant
b_2	Empirical constant
b_3	Empirical constant
c	A constant related to water binding energy to the primary binding sites
c_1	A dimensionless measure of the strength of water binding to the primary binding sites
d_{av}	Average pore size (nm)
dx/dt	Sorption rate
K	A constant related to the adsorption energies of multilayer adsorption sites
k	Rate coefficient (s^{-1})
m	Moisture content (%)
m_0	The monolayer moisture content (%)
m_a	The mass flow rate of process air ($kg\ s^{-1}$)
Q_{de}	Dehumidification capacity ($kg\ h^{-1}$)
$RMSE$	Root mean square error
R^2	The coefficient of determination
S_{BET}	BET surface area ($m^2\ g^{-1}$)
S_{BET}^*	BET surface area related to the mass of porous host matrix (silica gel) ($m^2\ g^{-1}$)
t_{de}	Dehumidification time (s)
V_t	Total pore volume ($cm^3\ g^{-1}$)
V_t^*	Total pore volume related to the mass of porous host matrix (silica gel) ($cm^3\ g^{-1}$)
w_{ai}	Inlet humidity ratios of the process air ($g\ g^{-1}$)
w_{ao}	Outlet humidity ratios of the process air ($g\ g^{-1}$)
$wt.\%$	Mass concentration of impregnating salts (LiCl) (%)
x	The equilibrium water sorption quantity ($g\ g^{-1}$)
x_t	Dynamic water sorption quantity ($g\ g^{-1}$)

Abbreviation

DCAS	Desiccant-coated aluminum sheets
DCHS	Desiccant-coated heat sink
SGCAS	Silica-gel-coated aluminum sheets
SG-L0	Silica gel
SG-L30	Silica gel–LiCl composite prepared in 30 wt.% of LiCl aqueous solution
SG-L35	Silica gel–LiCl composite prepared in 35 wt.% of LiCl aqueous solution
SG-L40	Silica gel–LiCl composite prepared in 40 wt.% of LiCl aqueous solution
SG-L45	Silica gel–LiCl composite prepared in 45 wt.% of LiCl aqueous solution

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