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Preparation of calcium chloride-anodized aluminum composite for water vapor sorption

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Abstract

In the present study, we propose a novel solid sorbent, which is composed of anodized aluminum and calcium chloride, for water sorption chillers and heat pumps. Aluminum is electrolyzed in acid baths with the result that a thin and porous aluminum oxide film is formed on its surface. The anodic alumina films prepared using an electrolytic bath of sulfuric acid have an average thickness from 8 to 100 μm and mean pore diameter from 6 to 22 nm. The physical properties of anodized aluminum can be controlled by electrolytic conditions such as current density, processing time and temperature. A calcium chloride-anodized aluminum composite sorbent has been prepared by a solution impregnating method. The amount of calcium chloride impregnated on the alumina films reaches up to 16.1 wt%, and the deposition of calcium chloride in the alumina layer has been confirmed by X-ray analysis. The experimental results shows that bare anodized aluminum adsorbs very little water vapor, but the prepared calcium chloride-anodized aluminum composite is active against water vapor even in the low pressure range. Hence, this composite is a promising sorbent for adsorption chillers and heat pumps using water as working fluid.

Keywords: Water vapor sorption, Composite sorbent, Anodized aluminum, Calcium chloride, Adsorption chiller

Nomenclature

A surface area of sample plate [mm^2]
 d_p mean pore diameter [nm]
 I current density [A/m^2]

L	thickness of sample plate [mm]
m	impregnated mass of calcium chloride [mg]
n	water uptake [mol/mol]
P	pressure [kPa]
q	amount sorbed [kg/kg]
q_s	saturation amount sorbed [kg/kg]
R	calcium chloride content in composite layer [%]
T	temperature [K]
w	weight of sample plate [g]

Greek symbols

δ	average film thickness [μm]
θ	time [min]
ρ_{Al}	density of aluminum [g/mm^3]
ϕ	relative pressure [-]

Subscripts

an	anodization
imp	impregnation
PWT	pore widening treatment

1. Introduction

Adsorption chillers and heat pumps using solid sorbent/refrigerant pairs are thermally-driven systems, and the low-temperature waste heat can be utilized as heat sources in the systems. Currently adsorption chillers with silica gel/water or zeolite/water pairs have been put to practical use but have not become widespread yet, because they are large and expensive when compared with LiBr/water absorption chillers. Since packed-bed adsorbers, where the heat transfer rate is very low, are employed in adsorption chillers, the cold heat energy output is controlled by the heat transfer rate in the packed bed. Commonly, many finned tubes are inserted into the bed for heat transfer enhancement, but they bring about enlargement of the size of the adsorber, i.e. adsorption chiller. Therefore, the further heat transfer enhancement in the adsorber is essential for downsizing adsorption chillers.

Aluminum is a light and highly heat-conductive metal, and is commonly used as a material for heat exchangers mounted in packed beds of particles. An aluminum plate is oxidized readily by electrochemical reactions in an acid bath, and an aluminum oxide film is formed on its surface [1,2]. Since the anodic alumina film has a porous structure, it can be a host matrix for impregnation with

some chemicals. Take et al. [3] have proposed to use anodized aluminum as a catalyst support and developed Cu-Zn/Al₂O₃/Al-plate and Pt/Al₂O₃/Al-plate catalysts for methanol steam-reforming reaction.

For adsorption chillers, some researchers have proposed consolidated beds of sorbent particles such as silica gel and zeolite over metal surfaces to enhance the heat transfer in the adsorbers [4-8]. These consolidated sorbent beds were prepared using some binders. Consequently, sorption sites for refrigerant vapor decrease.

If metal surfaces for heat exchange have the activity of water sorption, they will be very interesting materials not only for adsorption chillers but also for other sorption applications. The anodized aluminum impregnated with calcium chloride, which have hygroscopic nature, may meet this requirement. In this study, to obtain anodized aluminum with proper film structures to impregnation with calcium chloride, we examined the relationship between the physical properties of alumina films and the processing conditions for aluminum anodic oxidation and pore widening treatment. And then the anodized aluminum plates obtained were impregnated with calcium chloride by immersing them in a saturated aqueous solution of calcium chloride at atmospheric or reduced pressures. The prepared calcium chloride-anodized aluminum composites were examined for their sorption capacities for water vapor.

2. Experimental

2.1 Sample and pretreatments

In the experiments, we used an aluminum plate with a purity of 99.7 % as a base material, and the sizes were 90 mm long, 12 mm wide and 0.3 mm thick. In order to remove grease, naturally oxidized film and the other contaminants from the surface of the aluminum plate, the plate was subjected to the following pretreatment. First, the aluminum plate was soaked in 8 vol% aqueous solution of sulfuric acid at 293 K for 7 minutes. After washing the plate with distilled water, it was etched by using an aqueous solution of sodium hydroxide with a concentration of 60 g/l at 318 K for 5 minutes. After washing it with water again, the plate was kept in 5 vol% sulfuric acid solution at 293 K for 5 minutes. Finally, we rinsed the plate surface with distilled water.

2.2 Anodic oxidation and pore widening treatment

Figure 1 shows preparation procedures of the calcium chloride-anodized aluminum composite sorbents. The procedures are divided into three main processes: anodic oxidation, pore widening treatment and impregnation with calcium chloride (CaCl₂).

Anodic oxidation was applied to the area 41 mm long by 12 mm wide of the pretreated aluminum plate. The aluminum plate was set as an anode in a bath of 1.5 M sulfuric acid solution, and a stainless steel plate (SUS304) 50 mm long by 18 mm wide by 2 mm thick was used as a cathode.

The aluminum plate was anodized at a given time and temperature by applying a direct current with a constant density of 200-400 A/m². The electrolyte was fully stirred. By this treatment, aluminum is oxidized to form a porous thin layer of aluminum oxide on the plate surfaces.

Then the anodized aluminum plate was soaked in 2.25 M aqueous solution of sulfuric acid at 298 K for a given time in order to widen pores in the oxide film [9]. This is called pore widening treatment (PWT) in this study. Finally the sample plate was fired in an electric muffle furnace at 623 K for an hour to obtain the chemically stable anodic oxide film.

The thickness of anodic oxide film on the plate was measured using an eddy-current coating thickness tester (Kett Electric Lab., LH-330), and the diameter of pores in the film was determined from SEM (scanning electron microscope) images of the surface of the anodized aluminum plate.

2.3 Preparation of CaCl₂-anodized aluminum composite sorbent

A composite of calcium chloride and anodized aluminum was prepared by solution impregnation process. A saturated aqueous solution of CaCl₂ was employed as an impregnating solution. To keep the solution saturated during the impregnation process, calcium chloride in excess of its solubility was initially added to water. The anodized aluminum plate, which is a porous matrix, was soaked in a saturated aqueous solution of CaCl₂ under atmospheric or reduced pressure condition at room temperature. The sample plate was taken out from the solution after the elapse of a given time, and then calcination of the sample was carried out in a muffle furnace at 773 K for 3 hours. We have obtained CaCl₂-anodized aluminum composite sorbents in this procedure. The amount of calcium chloride impregnated on the anodized aluminum (*m*) was determined by the difference in mass before and after the impregnation. Calcium chloride content in the composite layer (*R_{imp}*) was defined as follows:

$$R_{\text{imp}} = \frac{m}{w_{\text{imp}} - \rho_{\text{Al}}(L_{\text{imp}} - 2\delta_{\text{imp}})A} \times 100$$

where *w_{imp}* and *L_{imp}* are the weight [g] and the thickness [mm] of impregnated sample plate respectively, and *δ_{imp}* is the thickness of composite layer [mm], *ρ_{Al}* is the density of aluminium [g/mm³], *A* is the surface area of sample plate [mm²].

The CaCl₂-anodized aluminum composites were examined for the characteristics of water vapor sorption with a magnetic suspension balance (MSB, Rubotherm Prazisionsmesstechnik) [10,11].

3. Results and discussion

3.1 Anodic oxide film

Figure 2 shows SEM images of the surface and cross section of anodic oxide film prepared at a current density (*I_{an}*) of 400 A/m² and a processing time (*θ_{an}*) of 60 minutes. The average thickness of the oxide film obtained is 32.2 μm. The oxide film has innumerable pores of diameter around 10 nm.

The pores open on the surface and develop in the direction of the film thickness. We confirmed that anodic oxide films with the same thickness are formed on both sides of the aluminum plate. This observation indicates that anodic aluminum oxide film has a structure suitable for impregnation with CaCl_2 .

Figure 3 shows the average film thickness (δ) and pore diameter (d_p) of anodized aluminum prepared at the different electrolytic current density and processing time. The film thickness increases with an increase in current density and/or processing time. Under experimental conditions employed in this study, the oxide films of 8.4-92.6 μm thickness are formed on the plate surfaces. For anodic oxidation of aluminum, oxide films are formed by the following electrochemical reactions [1].



Therefore, film formation depends on the quantity of electricity supplied to the aluminum plate. At high current density and/or long processing time, aluminum oxide film rapidly develops as shown in this figure.

On the other hand, the mean pore diameter also increases with an increase in current density and/or anodizing time. In the experiments, its value ranges from 6 to 16.4 nm. The development of pores relates closely to dissolution of aluminum oxide in acidic bath, where the following chemical reaction occurs [1].



For lengthy processing, anodic oxide films have been developing, but the film surface is exposed to strongly acidic electrolyte in the meantime. The pore walls in the oxide film gradually begin to dissolve and as a result the pore diameter would increase.

Figure 4 shows the effect of bath temperature for anodic oxidation (T_{an}) on the average film thickness and pore diameter of anodized aluminum. The current density is 400 A/m^2 and the processing time 80 min. There is a significant effect of the bath temperature on the film thickness and pore diameter. The average film thickness decreases gradually with an increase in bath temperature. On the contrary, the pore diameter increases linearly with an increase in temperature. Chemical reactions of both formation and dissolution of aluminum oxide film proceed simultaneously in the anodic oxidation process. When the formation rate is faster than the dissolution rate, anodic oxide film develops. That is, since the dissolution of aluminum oxide film is suppressed in the anodic oxidation at lower temperature, thicker oxide film with small-size pores is formed on the aluminum plate surfaces.

These results indicate that the physical properties of anodic oxide film are controlled by anodizing conditions such as current density, processing time and temperature. We confirmed that

the number of pores in anodic oxide film decreases with increasing current density and/or processing time. In the experiments, its value ranges from 5.3×10^{14} to $12.1 \times 10^{14} \text{ m}^{-2}$.

After anodic oxidation, the anodized aluminum plates were subjected to the pore widening treatment in sulfuric acid bath. Figure 5 shows the relationship between the mean pore diameter of anodic oxide film and immersion time in the bath. Anodized aluminum plates obtained by anodic oxidation at 400 A/m^2 and 288 K for 80 minutes were used for the PWT. At longer immersion time, the pores become enlarged. The mean pore diameter for 60 min PWT increases by approximately 1.5 times of that of anodized aluminum without PWT. We confirmed that the PWT has an insignificant effect on reduction of the film thickness, and the reduction ratio of the film thickness was below 2 percent in the PWT experiments.

3.2 CaCl_2 -anodized aluminum composite sorbent

The preparation conditions of CaCl_2 -anodized aluminum composite sorbents are listed in Table 1. As a matrix for impregnation with CaCl_2 we used anodized aluminum plates prepared under the two different conditions (anodized aluminum I: $\theta_{\text{an}} = 80 \text{ min}$, $I_{\text{an}} = 400 \text{ A/m}^2$, $T_{\text{an}} = 288 \text{ K}$, $\theta_{\text{PWT}} = 60 \text{ min}$, anodized aluminum II: $\theta_{\text{an}} = 40 \text{ min}$, $I_{\text{an}} = 300 \text{ A/m}^2$, $T_{\text{an}} = 293 \text{ K}$, $\theta_{\text{PWT}} = 60 \text{ min}$). The average film thickness of anodized aluminum I is $100.2 \text{ }\mu\text{m}$, and this value is larger than that of anodized aluminum II ($30.9 \text{ }\mu\text{m}$). The mean pore diameter of the former (21 nm) is roughly same as that of the latter (19 nm). Impregnation with calcium chloride was carried out using saturated aqueous solution of CaCl_2 at room temperature. Four different CaCl_2 -anodized aluminum composite sorbents (sample A, B, C and D) were obtained by soaking anodized aluminum I and II in the solution at atmospheric pressure for 24 hours or at reduced pressure for 3 hours.

Figure 6 shows the impregnated mass of CaCl_2 (m) for the four samples shown in Table 1. For impregnation at atmospheric pressure, the amount of CaCl_2 impregnated on sample A is somewhat larger than that on sample B. On the other hand, for impregnation at reduced pressure, the amount of CaCl_2 impregnated on sample C or D is significantly larger than that on sample A or B. In particular, the impregnation mass on sample C with the oxide film of $100.2 \text{ }\mu\text{m}$ reaches 46.8 mg . This value is 2.3 times as large as that for sample D and 3.7 times larger than that for sample A. This result can be interpreted as follows. Since anodized aluminum I (samples A and C) has a thicker porous film than anodized aluminum II (samples B and D), the surface area of anodized aluminum I for impregnation is larger than that of anodized aluminum II. Under reduced pressure, any remaining air in the pores is expelled, and then the solution impregnant penetrates deep into the pores. As a result, sample C has been impregnated with a large amount of calcium chloride.

We observed the surface and cross section of CaCl_2 -anodized aluminum composites using SEM and analyzed elements of the composite layers by an EDX (energy dispersive X-ray analysis) method. Figure 7 shows SEM image, EDX spectra and element mappings of aluminum, oxygen,

calcium and chlorine of the near-surface cross section of sample C. We cannot obviously observe calcium chloride crystals on the film surface and in the pores from the SEM image. However, the EDX spectra and element mappings demonstrate the presence of calcium and chlorine in addition to aluminum and oxygen which are constituent elements of aluminum oxide film. This result indicates that deposition of calcium chloride takes place not only on the surface but also in the pores of anodic oxide film. Impregnation at reduced pressure is effective means for preparation of CaCl₂-anodized aluminum composites.

3.3 Water vapor sorption

Figure 8 shows sorption isotherms of water vapor on CaCl₂-anodized aluminum composites at 303 K. Samples A and C were chosen in the water sorption experiments. The impregnated amount of CaCl₂ on the basis of the weight of composite layer (R_{imp}) is 5.7 wt% for sample A and 16.1 wt% for sample C. In the figure, adsorption isotherms for bare anodized aluminum I and commercial silica gel (Fuji Silysia Chem. Ltd, RD2560) are also shown for comparison purpose. The relative pressure (ϕ) in the horizontal axis means the ratio of vapor pressure in sorption equilibrium to a saturated one at measurement temperature. Bare anodized aluminum I has little capacity to adsorb water vapor in the relative pressure range below 0.55. On the other hand, the prepared CaCl₂-anodized aluminum composites sorb water vapor in this pressure range, and the amount sorbed (q) increases with increasing relative pressure. The amount sorbed on the 16.1%-composite (sample C) is obviously larger than that on the 5.7%-composite (sample A). However, the sorption capacity of the 16.1%-composite has not come up to that of silica gel. Thus, for practical application of the CaCl₂-anodized aluminum composite sorbents to adsorption chillers and heat pumps, an increase in amount of CaCl₂ impregnated on anodized aluminum will be required.

Figure 9 shows the relationships between water uptake (n) of CaCl₂-anodized aluminum composites and bulk CaCl₂, and the relative vapor pressure. The water uptake in vertical axis is the mole ratio of the sorbed water to calcium chloride. The water uptake for every sorbent levels off at around $n = 2$ and suddenly rises from $n = 2$ to 4. This result indicates that calcium chloride impregnated on anodized aluminum reacts with water primarily to give calcium chloride dihydrate and then to give calcium chloride tetrahydrate. The water uptakes of the 16.1%-composite and bulk CaCl₂ increase over $n = 6$, and in this range deliquescent of calcium chloride will occur.

The CaCl₂-anodized aluminum composite (15.9 wt%) and silica gel were examined for the water sorption rates. Compared in Fig. 10 are the time courses of the dimensionless amount of water vapor sorbed on these sorbents (q/q_s) at the relative pressure of 0.289 and the sorption temperature of 303 K. The saturation amount sorbed (q_s) is 0.138 kg/kg for 15.9%-composite and 0.192 kg/kg for silica gel. The vapor amount sorbed on the CaCl₂-anodized aluminum composite increases linearly just after starting the experiment and exceeds 70% of the saturation value after 20 minute. On the other

hand, the initial water sorption rate for silica gel is faster than that for the composite, and the amount sorbed effectively reaches the saturation value in 30 minute. A slow diffusion of water vapor in long and narrow spaces in composite layer would contribute to a decrease in water sorption rate. This result indicates that the heat transfer rate in the adsorber using the CaCl_2 -anodized aluminum composites may be controlled by the rate of water sorption on them.

4. Conclusions

The calcium chloride-anodized aluminum composite has been proposed as a novel solid sorbent for water vapor sorption. The anodized aluminum plate is prepared by aluminum electrolysis using sulfuric acid bath, and thin and porous oxide films are formed on its surface. The physical properties of anodic oxide films can be controlled by anodizing conditions such as current density, processing time and temperature. The anodic oxide films obtained in this experiment have a thickness from 8 to 100 μm and a pore diameter from 6 to 22 nm. The pores can be widened by immersion in sulfuric acid bath.

The calcium chloride-anodized aluminum composite sorbent has been prepared by the solution impregnating method. The deposition of calcium chloride occurs on the surface and in the pores of anodic oxide film, and the impregnated amount reaches up to 16.1wt%. The results of the sorption experiments show that bare anodized aluminum adsorbs very little water vapor, but the calcium chloride-anodized aluminum composite is active against water vapor even in the low pressure range. As a result, this composite is a promising sorbent for adsorption chillers and heat pumps using water as working fluid.

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Figures

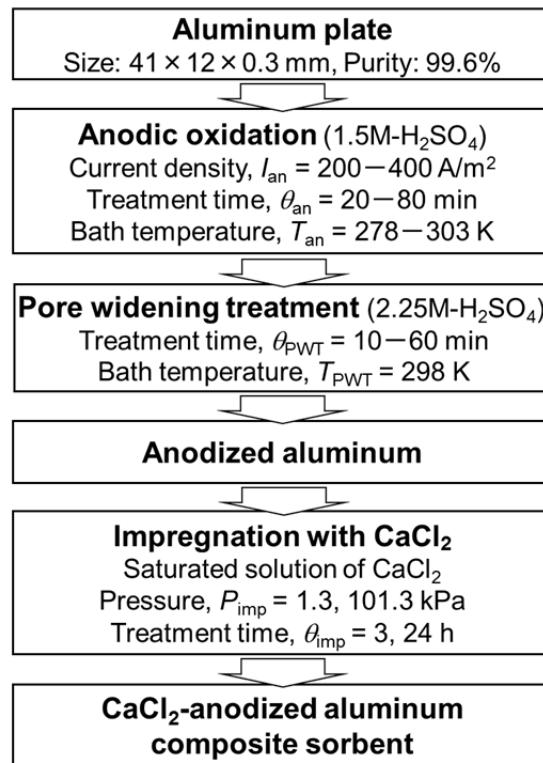


Fig. 1. Preparation procedure of CaCl₂-anodized aluminum composite sorbent.

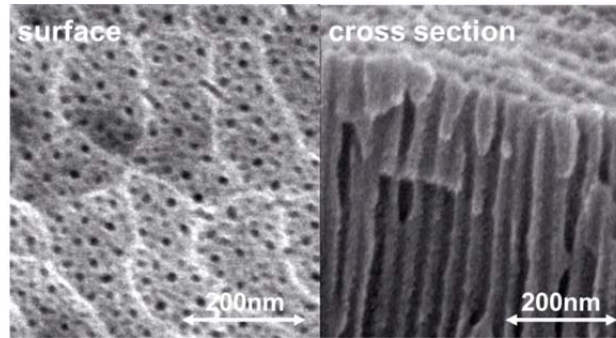


Fig. 2. SEM images of the surface and cross section of the prepared oxide film ($I_{an} = 400 \text{ A/m}^2$, $\theta_{an} = 60 \text{ min}$).

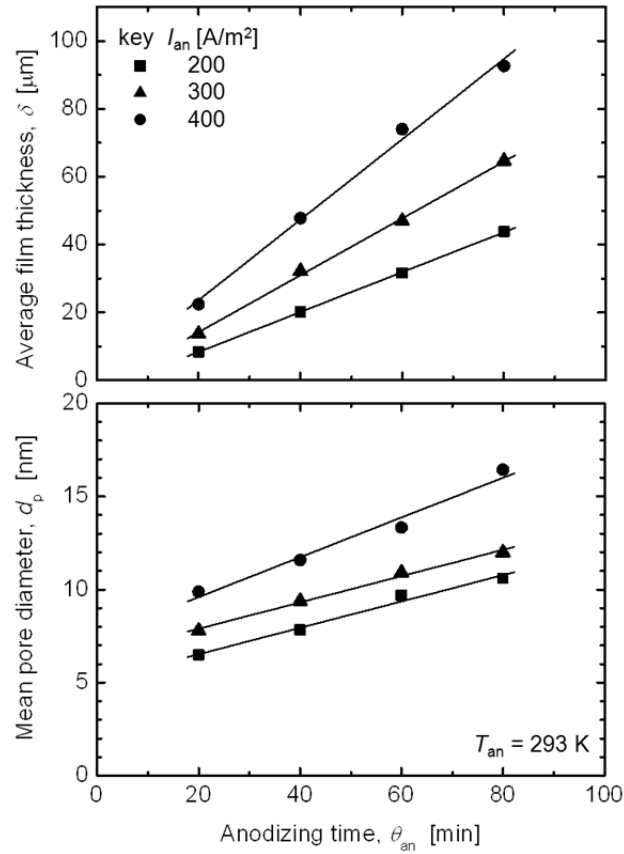


Fig. 3. Effect of current density and processing time on average film thickness and pore diameter of anodized aluminum ($T_{an} = 293$ K).

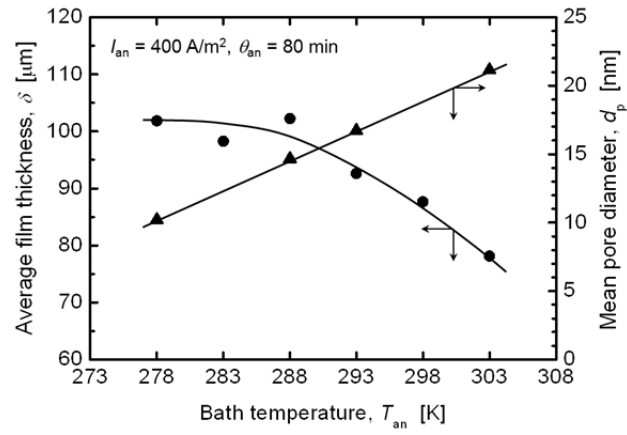


Fig. 4. Effect of bath temperature on average film thickness and pore diameter of anodized aluminum ($I_{an} = 400 \text{ A/m}^2$, $\theta_{an} = 80 \text{ min}$).

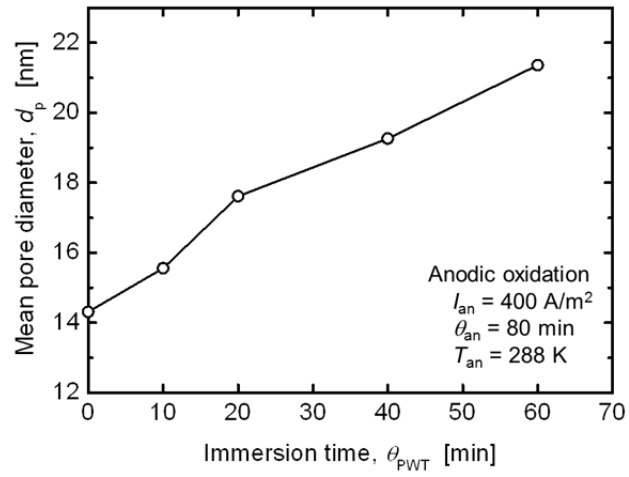


Fig. 5. Relationship between mean pore diameter of anodic oxide film and immersion time for PWT.

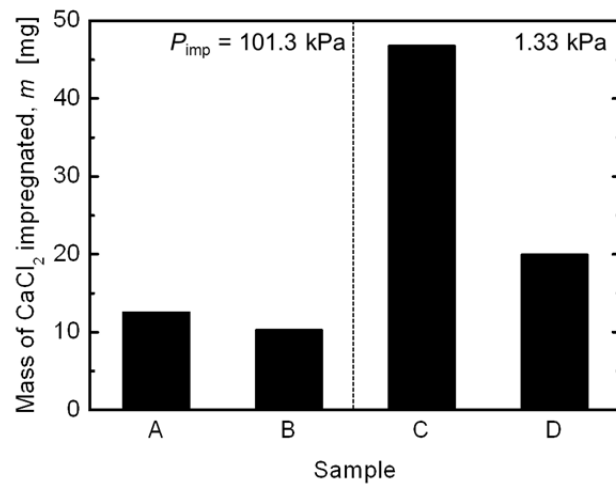


Fig. 6. Impregnated mass of CaCl₂ on samples A, B, C and D.

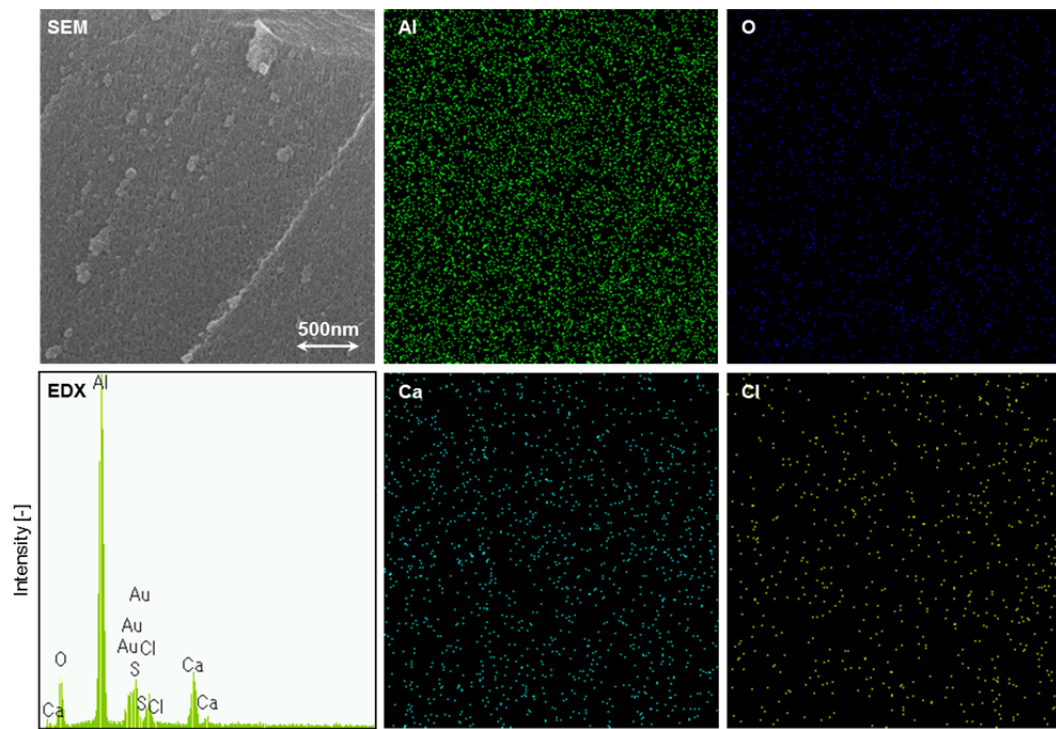


Fig. 7. SEM image, EDX spectra and element mappings of Al, O, Ca and Cl for the near-surface cross section of CaCl_2 -anodized aluminum composite layer (sample C).

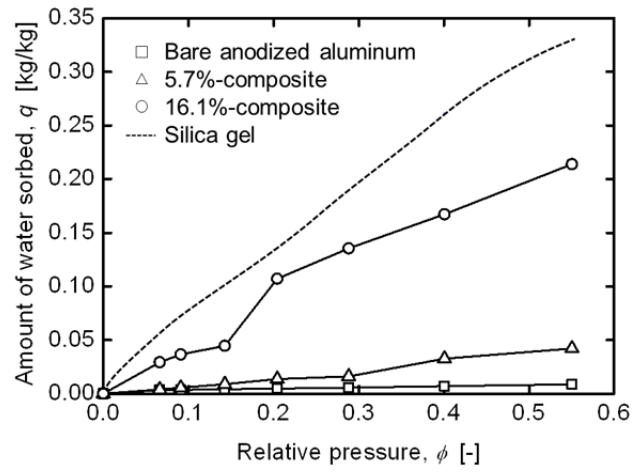


Fig. 8. Sorption isotherms of water vapor on CaCl_2 -anodized aluminum composites, bare anodized aluminum and silica gel at 303 K.

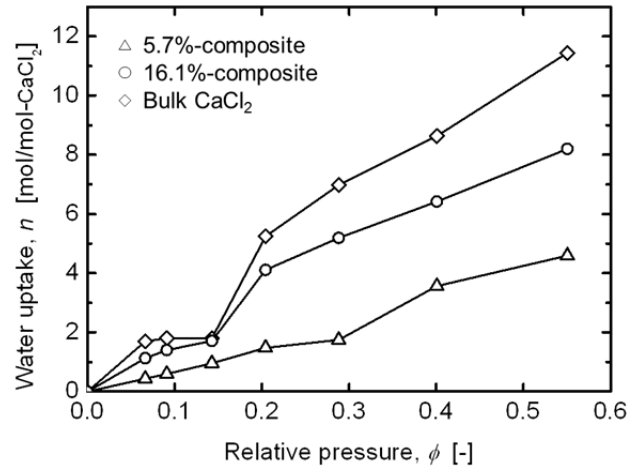


Fig. 9. Relationships between water uptake by CaCl_2 -anodized aluminum composites and bulk CaCl_2 , and relative pressure.

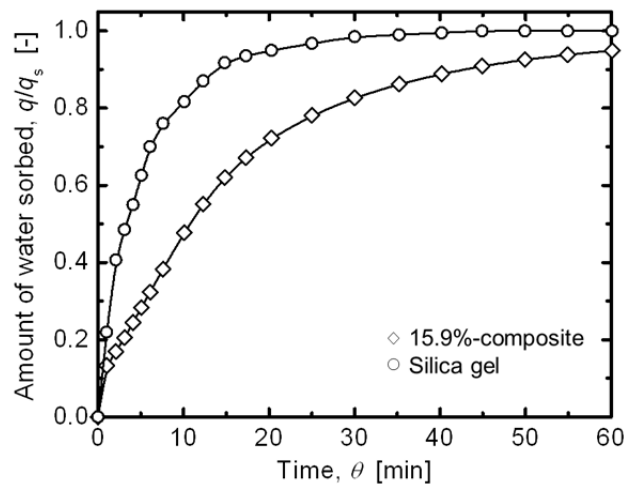


Fig. 10. Comparison of the time courses of the dimensionless amount of water vapor sorbed on CaCl_2 -anodized aluminum composite and silica gel.

Tables

Table 1 Preparation conditions of CaCl₂-anodized aluminum composite sorbents

Sample	A	B	C	D
Anodic oxidation				
θ_{an} [min]	80	40	80	40
I_{an} [A/m ²]	400	300	400	300
T_{an} [K]	288	293	288	293
Pore widening treatment				
θ_{PWT} [min]	60	60	60	60
Impregnation with CaCl ₂				
P_{imp} [kPa]	101.3	101.3	1.33	1.33
θ_{imp} [h]	24	24	3	3