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journal or publication title	Journal of Chemical Engineering of Japan
volume	49
number	3
page range	274-279
year	2016-03-20
URL	http://hdl.handle.net/2297/45518

doi: 10.1252/jcej.14we286

Water Vapor Sorption Characteristics of Calcium Chloride-Anodized Alumina Composites

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Keywords: Composite Sorbent, Calcium Chloride, Anodized Alumina, X-ray Diffraction, Water Vapor Sorption

In this study, calcium chloride–anodized alumina composites were examined for water vapor sorption properties. Porous alumina host matrices for calcium chloride impregnation were prepared by anodizing aluminum plates in an oxalic acid bath or a sulfuric acid bath. $CaCl_2$–alumina composites were obtained through calcination of the anodic alumina film impregnated with $CaCl_2$ solution at 473 or 773 K. XRD analyses indicated that the type of host matrix and the calcination temperature made an effect on crystal states of calcium chloride in the composite layer. The composite calcined at 473 K, of which host matrix was oxalic-acid anodized alumina film, contained calcium chloride anhydrate crystals. Water vapor sorption experiments showed that the composite with crystalline calcium chloride sorbed well water vapor, and its sorption isotherm had a shape similar to that of bulk $CaCl_2$. Therefore, the water sorption behavior of the $CaCl_2$–alumina composite strongly depends on crystal states of calcium chloride in anodized alumina layer.

Introduction

Metal salts such as calcium chloride, lithium chloride and calcium nitride have a high hygroscopic nature, and their sorption capacities of water vapor are larger than that of silica gel or zeolite. Water vapor sorption on metal salt contains a gas-solid reaction related to the formation of hydrates. According to the Gibbs's phase rule, the reaction between solid metal salt and water vapor is a monovariant system, that is, the sorption equilibrium can be determined by either the vapor pressure or the sorption temperature (Aristov, 2007). This property is desirable as working pair for sorption chillers. Many researchers have proposed to immobilize metal salts in porous materials such as silica gel (Aristov *et al.*, 1996a), alumina (Sharonov and Aristov, 2005) and expanded graphite (Fujioka *et al.*, 2008) to ensure easy handling of the metal-salt particles and/or to enhance the heat and mass transfer rates in solid-sorbent beds.

Aluminum is one of the most suitable materials for heat exchangers because of the high thermal conductance. If aluminum plates have the hygroscopic properties, they will be very attractive sorption materials that can be rapidly cooled and heated. In order to meet this requirement, we prepared aluminum plates with porous thin aluminum oxide films on both sides by anodizing in acidic baths, and then calcium chloride was deposited into pores of the films by a solution impregnation method in the previous works (Kumita *et al.*, 2013; Suwa *et al.*, 2014). The physical properties of alumina films such as the thickness and pore size varied depending on the type of electrolyte and anodizing conditions. Anodized alumina films prepared in oxalic acid bath had larger pores and higher porosity than those prepared in sulfuric acid bath. The impregnated mass of $CaCl_2$ increased with an increase in porosity of the film. Calcium chloride–anodized alumina composites showed sorption activity against water vapor in the relative pressure range below 0.29, in which conventional sorption chillers work. The water sorption capacities increased with the $CaCl_2$ impregnation mass. On the other hand, the water sorption equilibria for the composites were different from that for bulk $CaCl_2$. The sorption isotherm of water vapor on bulk $CaCl_2$ at 303 K showed a plateau corresponding to the formation of calcium chloride dihydrate in the relative pressure range from 0.07 to 0.14, but the water vapor uptakes for the composites increased monotonically within this pressure range. Moreover, for some composites the amounts sorbed were obviously smaller than that for bulk $CaCl_2$ at a relative pressure of around 0.29. These are unfavorable behaviors for sorption refrigeration.

There are many papers on sorption equilibria of refrigerant vapor on metal-salt composite. For water/$CaCl_2$–silica gel system (Aristov *et al.*, 1996a, 1996b) and ammonia/$BaCl_2$–γ-alumina system (Veselovskaya *et al.*, 2010), metal salts confined into solid host matrices had sorption characteristics different from bulk ones. Some researchers reported that the sorption isotherms or isobars for metal salt composites had not stepwise shapes but linear shapes when metal salts were deposited in pores smaller than

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Received on ⋯
DOI: ⋯
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15 nm (Gordeeva *et al.*, 2002; Simonova *et al.*, 2009; Tokarev *et al.*, 2010; Yu *et al.*, 2014). Furthermore, Gordeeva *et al.* (2005) observed the formation of amorphous calcium chloride in pores of nanoporous silica gel when the composite was prepared through calcination at a relatively-high temperature after solution impregnation. The amount of water vapor sorbed on amorphous calcium chloride increased monotonously with the relative vapor pressure. They indicated that the formation of amorphous calcium chloride was associated with the interfacial interaction between calcium chloride and the pore surface of silica gel. For silver halide–alumina composite electrolytes, amorphous silver halide was formed on the surface of alumina nanoparticles by a high-temperature treatment (Maier, 1985; Uvarov *et al.*, 2000).

In light of these research findings, it is important to investigate the crystal states of calcium chloride confined into anodized alumina film and the water-vapor sorption characteristics of our proposed composites. In this study, we prepared $CaCl_2$–alumina composites at different calcination temperatures using oxalic acid-anodized alumina and sulfuric acid-anodized alumina and examined the effects of the type of host matrix and the calcination temperature on the water vapor sorption equilibria.

1. Experimental

1.1 Anodic oxidation and pore widening treatment

An aluminum plate with a purity of 99.7% (The Nilaco Co.) was used as a base material, and the dimensions were 80 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 pretreated as follows. The aluminum plate was degreased with 8 vol% sulfuric acid solution at 293 K for 7 min. After washing the plate with distilled water, it was etched by using a 60 g/*l* aqueous solution of sodium hydroxide at 318 K for 5 min. After washing it again, the plate was kept in a 5 vol% sulfuric acid solution at 293 K for 5 min.

Anodic oxidation was applied to a rectangular area of 41 mm long by 12 mm wide on the pretreated aluminum plate. The aluminum plate was set as an anode in either a 0.45 M oxalic acid bath or a 1.5 M sulfuric acid bath, and a stainless steel plate (SUS304) of 50 mm long by 18 mm wide by 2 mm thick was used as a cathode. The aluminum plate was anodized by applying a direct current with a constant density (I_{an}) from a DC-supply (EX-375H2, Takasago Ltd.). During anodizing the electrolyte solution in a bath was fully stirred. Porous thin aluminum oxide films were formed on the both sides of the plate through this treatment.

Then, in order to widen pores in the oxide film, the anodized plate was immersed in a 2.25 M sulfuric acid solution at a given time (θ_{PWT}) and temperature (T_{PWT}). Finally, the sample plate was calcined in an electric muffle furnace at 623 K for an hour to stabilize the chemical state of the aluminum oxide film.

The thickness of anodic oxide film on the plate (δ) was measured using an eddy-current coating thickness tester (LH-330, Kett Electric Lab.), and the total thickness of the sample (L) was measured using a micrometer (MDQ-30M, Mitutoyo Co.). The diameter and the number of pores in the film were determined from SEM images of the surface of anodized aluminum plate. The apparent density of anodic alumina film (ρ_{a}) was calculated from Eq. (1).

$$\rho_{\mathrm{a}} = \frac{m_{\mathrm{sample}} - \rho_{\mathrm{Al}}(L-2\delta)A}{2\delta A} \tag{1}$$

Here, m_{sample} is the mass of anodized sample plate, A the surface area of sample plate, and ρ_{Al} the density of aluminum.

1.2 Impregnation of anodized alumina film with $CaCl_2$

Calcium chloride impregnation into anodized alumina film was performed by a solution impregnation process with a saturated aqueous solution of $CaCl_2$. To promote the penetration of solution into pores, the impregnation was conducted under reduced pressure at 303 K (T_{imp}). After the two-hour immersion (θ_{imp}), the plate was taken out from the solution, and residual solution of $CaCl_2$ over the sample surface was removed by centrifugation at 900 rpm for 3 min. Then the sample plate was calcined at either 473 K or 773 K (T_{c}) for 3 h to obtain calcium chloride–anodized alumina composite sorbent.

The amount of calcium chloride impregnated in the composites (m) was determined by the change in sample weight before and after impregnation. $CaCl_2$ content in the composite layer was calculated from Eq. (2).

$$R_{\mathrm{imp}} = \frac{m}{m + 2\rho_{\mathrm{a}}\delta A} \times 100 \tag{2}$$

1.3 Characterization of $CaCl_2$–anodized alumina composites

Calcium chloride–anodized alumina composites were analyzed for the phase composition by X-ray diffraction (XRD) using an X-ray diffractometer (MiniFlex600, Rigaku Co.) through the 2θ range from 10 to 100 degrees. A monochromatic Cu Kα radiation was employed. The composite plate was enclosed in a polyimide bag with a film thickness of 7.5 μm in a nitrogen atmosphere to prevent the deposited calcium chloride from deliquescence.

The contents of calcium and chlorine in $CaCl_2$– alumina composite layer were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES). Approximately 90 mg of $CaCl_2$–anodized alumina composites were completely dissolved with a 1 M nitric acid solution at 338 K. In order to convert total chlorine ions in the solution into hardly-soluble silver chloride, an excessive amount of 0.1 M silver nitrate solution and deionized water were added. The silver chloride was removed from the solution by filtration with a membrane filter. The filtrate containing silver and calcium ions was diluted with a 0.6%

nitric acid solution. Then, the solution obtained was analyzed by ICP spectrometry to determine the quantities of silver and calcium ions. The amount of chlorine ion in the solution in which the composite was dissolved was calculated from the difference in content of silver ion in the initial solution and the analysis solution.

We confirmed that the impregnated mass of calcium chloride determined from the ICP data gave close agreement with that determined by weighing method described above within an error of 5%.

1.4 Evaluation of water vapor sorption capacity

Calcium chloride–anodized alumina composites were evaluated for the water vapor sorption capacities by using a volumetric measuring apparatus. At the beginning, water sorbed on the sample was removed by vacuum dehydration at 353 K. After confirmation that the change in pressure in a measuring chamber was stabilized within 1 Pa, we began sorption experiments. The water vapor pressure in the chamber was controlled by the temperature of an evaporator and was monitored with a sapphire capacitance diaphragm gauge (SPG5A, Azbil Co.).

2. Results and Discussion

2.1 Calcium chloride impregnation

Figure 1 illustrates the relationship between the impregnated mass of $CaCl_2$ per unit apparent volume of the anodic oxide film (m_{imp}) and the apparent density of the film (ρ_a). The porous alumina host matrices were prepared by oxalic acid anodizing or sulfuric acid anodizing. We prepared some anodized alumina host matrices with different apparent densities by changing the pore widening treatment (PWT) time. All the composites were obtained through calcination at 473 K after $CaCl_2$ impregnation. Figure 1 shows negative correlation between the impregnated mass of $CaCl_2$ and the apparent density, regardless of the types of host matrices. The composite layer with higher apparent density means the same thing as that with higher porosity. Therefore, the impregnated mass of $CaCl_2$ could be controlled by the apparent density, i.e., the porosity of the anodic oxide film.

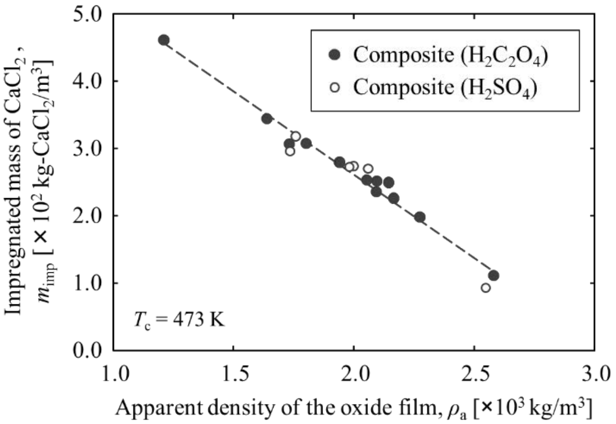

Fig. 1 Relationship between impregnated mass of $CaCl_2$ onto anodic alumina film and apparent density of the film.

We prepared four kinds of $CaCl_2$–anodized alumina composites to examine them for the physical properties of porous alumina host matrix and for the characteristics of $CaCl_2$ impregnation and water vapor sorption. The anodized alumina films before $CaCl_2$ impregnation were roughly the same in apparent density of 2.0×10^3 kg/m^3. **Table 1** shows the preparation conditions for the four composites. A sample codes were given to the composites according to the type of electrolyte for anodic oxidation and the calcination temperature after $CaCl_2$ impregnation.

Figure 2 shows SEM images of the surface of the anodic oxide films prepared in the oxalic acid bath (A) and the sulfuric acid bath (B). Both of the samples were subjected to the pore widening treatment for 600 min (A) or 90 min (B) after anodic oxidation. The mean pore diameter in alumina film A (D_{pm} = 85 nm) is obviously larger than that in alumina film B (D_{pm} = 15 nm). On the other hand, alumina film B has a number density of 4.9×10^{14} m^{-2}, and this value is approximately 10 times greater than for alumina film A (5.1×10^{13} m^{-2}). Assuming that the pores have cylindrical shapes, the surface areas of pore wall per unit apparent volume of alumina films A and B were estimated to be 1.4×10^7 and 2.3×10^7 m^2/m^3, respectively.

Figure 3 shows the calcium chloride content in the composite layer of the four samples. Composites Oxal473, Oxal773 and Sulf473 are about the same in content of $CaCl_2$, but Composite Sulf773 has an extremely-low content of

Table 1 Preparation conditions of four kinds of $CaCl_2$-anozied alumina composites.

Sample code		Oxal473	Oxal773	Sulf473	Sulf773
Electrolyte		$H_2C_2O_4$	$H_2C_2O_4$	H_2SO_4	H_2SO_4
θ_{an}	[min]	240	240	60	60
I_{an}	[A/m^2]	200	200	400	400
T_{an}	[K]	293	293	288	288
θ_{PWT}	[min]	600	600	90	90
T_{PWT}	[K]	293	293	293	293
θ_{imp}	[min]	120	120	120	120
T_{imp}	[K]	303	303	303	303
T_c	[K]	473	773	473	773

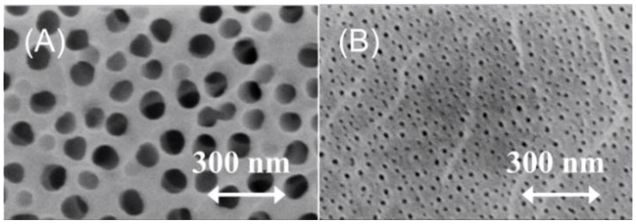

Fig. 2 SEM images of the surfaces of anodic alumina films prepared in oxalic acid bath (A) and sulfuric acid bath (B).

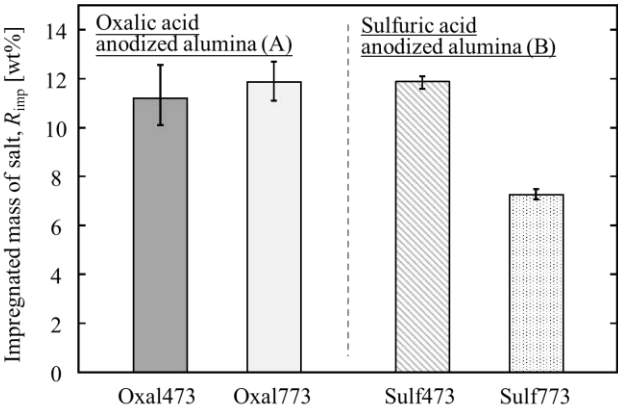

Fig. 3 $CaCl_2$ contents in composite layers of the four samples.

$CaCl_2$. This result suggests that the type of alumina host matrix and the calcination temperature would make a strong impact on the $CaCl_2$ impregnation characteristics.

2.2 Characterization of $CaCl_2$–anodized alumina composites

We conducted thermo-gravimetric (TG) analyses of Composites Oxal473 and Sulf473. The analyses were carried out in an air stream, and the samples were heated up to 773 K at 5 K/min. **Figure 4** shows the TG curves for the composites and saturated aqueous solution of calcium chloride. We confirmed that the mass of a bare alumina sample did not change in this temperature range. The mass of the $CaCl_2$ solution decreases by evaporation of solvent water and dehydration of precipitated $CaCl_2$ in the temperature range from 330 K to 450 K, and there is little change in mass above 450 K. The TG curve for Composite Oxal473 has a similar shape to that of the $CaCl_2$ solution. On the other hand, the mass change tendency for Composite Sulf473 is different from that for Composite Oxal473. Its mass decreases exponentially up to around 450 K and becomes stable. Then, it constantly declines in the temperature range above 650 K. These results indicate that the loss of impregnated mass for Composite Sulf773 would take place in the calcination process at a relatively-high temperature after $CaCl_2$ impregnation.

In order to find out the cause of the difference in the impregnated mass of salt between Composites Sulf773 and Oxal773, these composites were investigated the chemical compositions of salt deposited in the alumina films by ICP-OES. **Figure 5** shows the molar ratio between chlorine and calcium (Cl/Ca) in the composite layers of Composites Oxal773 and Sulf773. The value of Cl/Ca for Composite Oxal773 is close to 2, indicating that the salt deposits are calcium chloride. However, the molar ratio for Composite Sulf773 is approximately 1. Therefore, all of the salt deposits in the composite layer for Sulf773 would not be calcium chloride. These results suggest that the difference in the amount of salt deposit between Sulf773 and Oxal773 as shown in Fig. 3 is attributed to the fact that some chlorine leaves from calcium chloride in pores of the alumina film during the high-temperature calcination. The loss of chlorine would be linked to the formation of tricalcium aluminate for Composite Sulf773 to be hereinafter described.

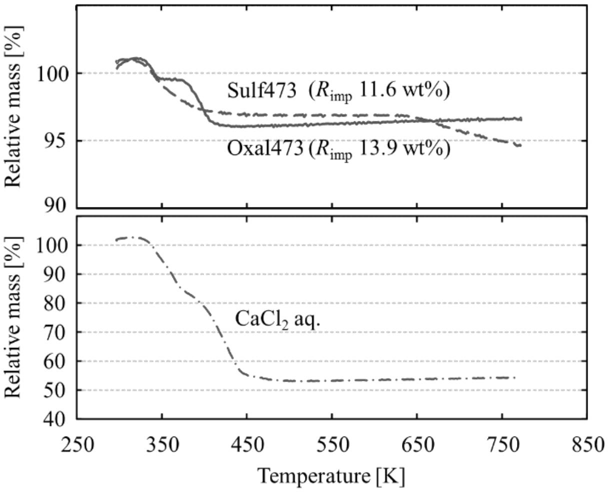

Fig. 4 Thermo-gravimetric curves for the $CaCl_2$–alumina composites and bulk $CaCl_2$.

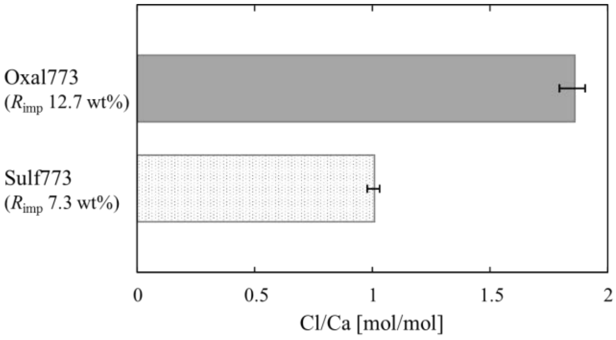

Fig. 5 Mole ratio of Cl/Ca in the composite layer.

Figure 6 shows the XRD patterns of the four $CaCl_2$–anodized alumina composites, bare anodized alumina substrates, and calcium chloride recrystallized from its aqueous solution. There is little clear diffraction peak other than aluminum ones for bare anodized alumina film, as also reported by Wang *et al*. (2005). Therefore, the bare alumina film consists almost of amorphous aluminum oxide. For Composite Oxal473, clear diffraction peaks corresponding to calcium chloride anhydrate are observed. On the other hand, the peak at 15.9 degrees for Oxal773 roughly agrees with one of the diffraction peaks of calcium chlorate $Ca(ClO_3)_2$. The peaks at 30.8 degrees for Oxal773 and ones at 43.8 and 45.7 degrees for Sulf473 correspond to that of calcium dialuminate $CaO \cdot 2Al_2O_3$. However, such XRD information is too little to conduct exact crystal identification. Since the

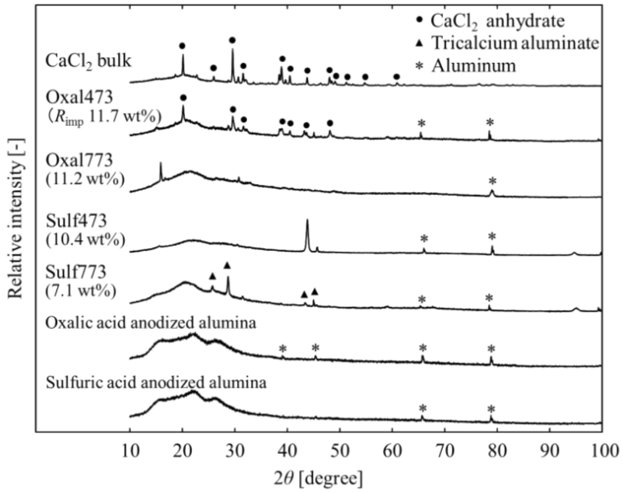

Fig. 6 X-ray diffraction patterns of the calcium chloride-anodic alumina composites, bare anodized alumina substrates, aluminum substrate and $CaCl_2$ bulk.

composites of Oxal773 and Sulf473 contain nearly the same amount of calcium chloride as Composite Oxal473, the chemical compositions of salt deposits are almost the same in every composite. Therefore, calcium chloride in Oxal773 and Sulf473 would be amorphous phase. The formation of amorphous metal salt is considered to be associated with the interfacial interaction, i.e., adsorption of metal cation onto the oxide surface during solution impregnation (Gordeeva *et al.*, 2005). Uvarov (1996, 2000) also reported that for metal salt–alumina composites, the peak intensities of crystalline salt weakened with an increase in mole fraction of alumina nanoparticles. This indicates that the formation of amorphous phase of salt is promoted when the metal salt–alumina interfacial area increased. Since the surface area of pores in sulfuric-acid anodized alumina was larger than that in oxalic-acid anodized alumina as shown in Fig. 2, the crystallization of calcium chloride might be suppressed in Composite Sulf473 compared to Composite Oxal473. For Composite Sulf773, the diffraction peaks of tricalcium aluminate $3CaO\cdot Al_2O_3$ are observed, indicating that a chemical reaction between calcium chloride and aluminum oxide might occur on its pore wall. Once tricalcium aluminate is formed, chlorine gas should be produced from surplus chlorine in the impregnant during calcination. As a result, the amount of calcium chloride deposit in Sulf773 was reduced as shown in Figs. 3 and 5.

These results indicate that the phase and chemical compositions of calcium chloride in anodized alumina layers are affected by the type of electrolyte for anodizing and by the calcination temperature after $CaCl_2$ impregnation.

2.3 Water vapor sorption

We examined the four $CaCl_2$–alumina composites for the water vapor sorption behaviors. **Figure 7** shows the sorption isotherms of water vapor on the composite sorbents at 303 K. For comparison, the sorption isotherm of bulk calcium chloride (Kanto Chemical Co., Inc.) is also shown in this figure. The water uptake *n* is the molar ratio of the sorbed water to calcium chloride. $CaCl_2$ bulk salt has plateaus with water uptake $n = 2$ in the relative pressure range from $\varphi = 0.03$ to 0.15 and $n = 4$ at $\varphi = 0.17$–0.2, which indicates the formation of stable crystalline hydrate $CaCl_2\cdot 2H_2O$ and $CaCl_2\cdot 4H_2O$ respectively. Composite Oxal473 sorbs much water vapor like bulk $CaCl_2$, and the water uptake rises sharply from $n = 2$ to 4 at a relative pressure of 0.16. This result indicates that the crystal state of calcium chloride in Composite Oxal473 is close to that of bulk $CaCl_2$. The amounts sorbed for Composites Oxal773 and Sulf473 increase monotonically with the relative pressure and their water sorption capacities are obviously smaller than those of Composite Oxal473 and bulk $CaCl_2$. These sorption behaviors imply that calcium chloride in Composites Oxal773 and Sulf473 has amorphous phase. Gordeeva *et al.* (2005, 2006) reported that the water sorption isotherm for crystalline calcium chloride in nanopores showed a stepwise pattern, but for amorphous salt the sorption isotherm became a linear shape. Composite Sulf773 with tricalcium aluminate poorly sorbs water vapor. As just described, the crystal states of calcium chloride confined into anodized alumina films have a significant effect on the water-vapor sorption characteristics. The effective amounts sorbed at $\varphi = 0.09$–0.29 are 4.4 mol/mol for Oxal473, 3.2 mol/mol for Oxal773, 2.3 mol/mol for Sulf473 and 0.8 mol/mol for Sulf773. Composite Oxal473 with crystalline calcium chloride has the highest sorption performance of water vapor in the four composites prepared in this study.

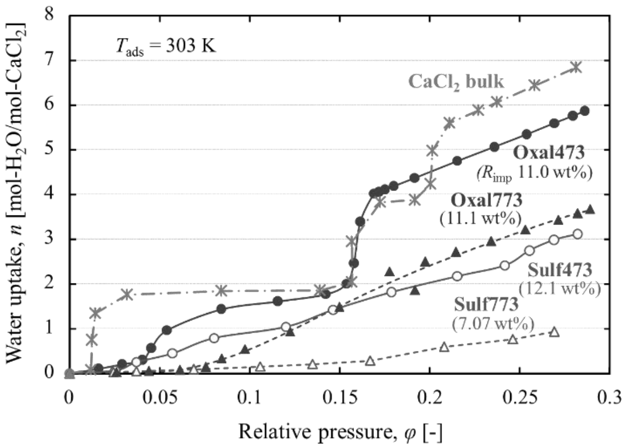

Fig. 7 Sorption isotherms of water vapor on $CaCl_2$–anodic alumina composites and $CaCl_2$ bulk at 303 K.

3. Conclusions

Aluminum plates were anodized in either a sulfuric acid bath or an oxalic acid bath to form porous and thin aluminum oxide films on the both sides of the plate. Saturated aqueous solution of calcium chloride was penetrated into porous alumina layers at reduced pressure, and then $CaCl_2$–alumina composites were obtained after calcination the $CaCl_2$ solution-soaked samples at a temperature of 473 or 773 K. XRD analyses showed that the calcination temperature after $CaCl_2$ impregnation significantly affected crystal states of calcium chloride deposited on aluminum oxide. For Composite Oxal473, there are X-ray diffraction peaks corresponding to calcium chloride anhydrate. On the other hand, there are no clear diffraction peaks corresponding to calcium chloride for Composites Oxal773 and Sulf473. Therefore, amorphous calcium chloride would be formed on these composites. The existence of tricalcium aluminate on Composite Sulf773 was confirmed through XRD analysis, indicating that calcium chloride reacted with alumina pore wall during the calcination process. Water sorption experiments showed that Composite Oxal473 had large capacity for water vapor sorption in the relative pressure range below 0.3 and that its sorption isotherm was similar to that for bulk calcium chloride. Water uptakes for Composites Sulf473 and Oxal773 monotonically increased with an increase in relative pressure, and their sorption capacities were obviously smaller than that for Composite Oxal473. Composite Sulf773 containing tricalcium aluminate had the poorest ability to sorb water vapor in the four samples. Therefore, water sorption behavior of the $CaCl_2$–anodized alumina composite strongly depends on crystal states of calcium chloride on the alumina pore surfaces. From these experimental results, the type of alumina host matrix and the calcination temperature after $CaCl_2$ impregnation are important factors to prepare $CaCl_2$–anodized alumina composites more suitable for water-vapor sorption refrigeration.

Nomenclature

A = Surface area of sample plate [m^2]
D_{pm} = Mean pore diameter [nm]
I_{an} = Current density [A/m^2]
L = Thickness of sample plate [m]
m = Amount of calcium chloride impregnated [kg]
m_{imp} = Impregnated mass of $CaCl_2$ per apparent volume of anodic alumina film [kg/m^3]
m_{sample} = Mass of anodic alumina plate [kg]
n = Molar ratio of sorbed water to calcium chloride [mol/mol]
R_{imp} = Salt content in the composite layer [wt%]
T_c = Calcination Temperature [K]
T_{imp} = Impregnation Temperature [K]
T_{PWT} = Pore widening treatment temperature [K]
δ = Thickness of anodic alumina film [m]
θ_{an} = Anodizing time [min]
θ_{imp} = Impregnation time [min]
θ_{PWT} = Pore widening treatment time [min]
ρ_{Al} = Density of aluminum [kg/m^3]
ρ_a = Apparent density of anodic alumina film [kg/m^3]
φ = Relative pressure [-]

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