



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.

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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.

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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 [μ m]
θ	time [min]
ρ_{Al}	density of aluminum [g/mm ³]
ϕ	relative pressure [–]
Subscripts	
an	anodization
imp	impregnation
PWT	pore widening treatment

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 min. 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 min. After washing it with water again, the plate was kept in 5 vol% sulfuric acid solution at 293 K for 5 min. Finally, we rinsed the plate surface with distilled water.

2.2. Anodic oxidation and pore widening treatment

Fig. 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

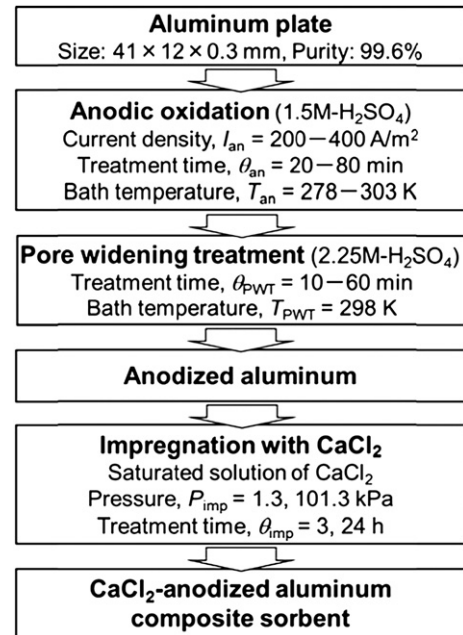


Fig. 1. Preparation procedure of CaCl₂-anodized aluminum composite sorbent.

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 h. 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:

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

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 aluminum [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].

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