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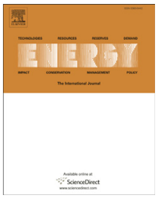

New composite sorbents of water and methanol “salt in anodic alumina”: Evaluation for adsorption heat transformation

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ABSTRACT

Development of new adsorbents of water and methanol specialised for AHT (adsorption heat transformation) can essentially advance this emerging low-carbon technology. This paper addresses the synthesis of novel composite sorbents based on an AA (anodic alumina) layer impregnated with hygroscopic salts, and the study of their ability to sorb water and methanol vapours. This work consists of the three parts: (1) synthesis and comparison of AA/Al sandwiches obtained with various electrolytes (sulphuric, oxalic, and phosphoric acids); (2) preparation of salt/AA composites (salt = $CaCl_2$ and LiCl) and study of their sorption equilibrium and dynamics with water and methanol vapours; and (3) evaluation of the new sorbents feasibility for AHT applications. The results obtained show that a) the new AA-based composites could be interesting for making compact AHT units with short working cycles, and b) still more R&D are necessary for further progress towards practical implementation of the new sorbents.

1. Introduction

Due to its high energy saving potential and the usage of environmentally benign working fluids AHT (Adsorption Heat Transformation) driven by low temperature heat is considered to be promising for cooling/heating applications [1–3]. Despite significant progress achieved in AHT for the last decades [4], further improvement of the transformation efficiency and, especially, the specific cooling power is still necessary for AHT successful implementation [1,5]. The power is essentially determined by a coupled heat and mass transfer in the “adsorbent – heat exchanger” unit. Therefore, new adsorbents that have advanced heat and mass transfer parameters together with good adsorption properties harmonized with particular AHT cycles are highly welcome [5–7].

An anodic aluminium oxide, or AA (anodic alumina), was first suggested for AHT in Ref. [8]. The AA formation by anodic oxidation of an aluminium sheet proceeds by the overall reaction [9]

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2. \tag{1}$$

The thickness of porous AA layers can reach several hundred microns [10,11]. The layer has a nearly regular texture with an array of straight-lined parallel pores which are perpendicular to the Al base and closed on the sheet side (Fig. 1). The pore texture is determined by anodization conditions, namely, the voltage of direct current and oxidation duration [9].

The AA layer is synthesized by a direct Faraday anodization of an aluminium sheet or foil that could be an element of real HEx (heat exchanger) used for AHT. In this case, a tight contact of the oxide layer with the aluminium HEx can be obtained (Fig. 1). This may significantly facilitate the heat transfer between the oxide layer served as adsorbent, and the metal directly contacted with a heat carrying fluid. Mass transfer to the oxide internal surface seems to be favourable in this geometry as well, due to open straight pore channels of the AA layer: the pore system is unbranched, thus, having no tortuosity and inaccessible sites (Fig. 1a). Thus, such sophisticated layer geometry was expected to be strongly advantageous because two main components of an AHT unit, which are a heat exchanger and an adsorbent bed, are combined in a single physical and chemical structure, namely, the AA/Al sandwich.

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Nomenclature

CC	cooling capacity, kJ/m^2
D_{kn}	Knudsen diffusivity coefficient, m^2/s
d	average pore diameter, μm
ΔH_e	evaporation heat of water/methanol, kJ/g
L	pore length (layer thickness), μm
l	free path of water molecules, μm
M	molecular mass of gas, g/mol
N	amount of adsorbed/desorbed water(methanol), mol/mol
N_p	pore density, m^{-2}
P	pressure, mbar
S	area of heat exchange, m^2
T	temperature, K
T_c	condenser temperature, K
T_e	evaporator temperature, K
T_d	regeneration temperature, K
T_{fin}	final temperature in dynamic experiment, K
T_{in}	initial temperature in dynamic experiment, K
t	time, s
t_s	electrolysis duration, h
V	volume of pores in the layer, cm^3/m^2
W_{max_ads}/W_{max_des}	maximum cooling power of adsorption/desorption stage, W/m^2
$W_{0.7}$	cooling power corresponding to 70% of the final conversion, W/m^2
Δw	amount of adsorbed/desorbed water(methanol), g/m^2
w_{max}/w_{min}	maximum/minimum uptakes, g/m^2

Greek letters

α	heat transfer coefficient, W/(m^2·K)
σ	effective diameter of a water molecule
τ	characteristic time, s
$\tau_{0.7}$	duration of adsorption/desorption stage corresponding to 70% of the final conversion, s
χ	conversion

Abbreviations

AA	Anodic Alumina
AC	Adsorptive Cooling
AHT	Adsorption Heat Transformation
EDX	Energy-Dispersive X-ray spectroscopy
HEx	Heat Exchanger
LTJ	Large Temperature Jump

Applicability of porous AA adsorbent synthesized by anodization of Al heat transfer plate for AC (adsorptive cooling) was studied in Ref. [12]. It was found that a maximal amount of water adsorbed by the AA layer at the relative humidity $P/P_o = 0.3$ is less than 0.07 kg/kg. Even lower water adsorption on AA layer was reported in Ref. [8]. It is known that for well-designed adsorptive chillers, the efficiency approaches acceptable values if the amount of water exchanged in the AC cycle exceeds (0.10–0.15) g/g [13]. To increase this value, deposition of a hydroscopic salt ($CaCl_2$) inside the AA pore space was performed in Refs. [8,14,15]. The AA layers were synthesized in aqueous solutions of sulphuric [8,14] and oxalic [15] acids as electrolytes. The layers exhibited the thickness $L \leq 100$ μm and the pore diameter $d = 5–40$ nm. It was shown that at a higher $CaCl_2$ content a larger amount of water was sorbed.

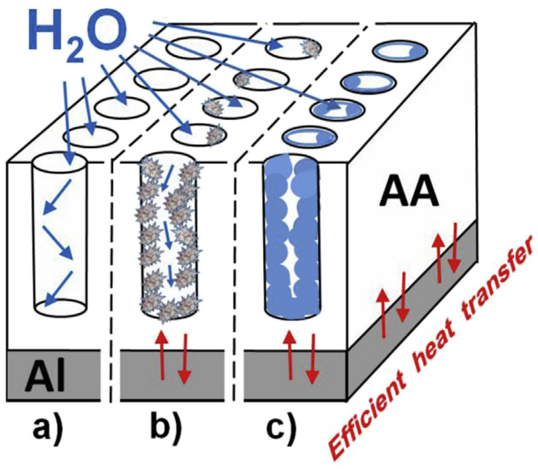

Fig. 1. Schematic fragments of AA layer: a – before impregnation; b – with dry salt, c – with hydrated salt. The latter fragment demonstrates possible blockage of the straight-lined AA pores due to the salt hydration.

In this work, next important steps towards evaluation of "salt – AA" composites for AHT were made. Firstly, we have varied the anodization conditions, namely, the electrolytes (sulphuric, oxalic, and phosphoric acids) and the duration, to optimize the AA texture (thickness, pore size and volume). We studied a new system – lithium chloride (LiCl) and methanol (CH_3OH) as active salt and sorptive, respectively. The system "$CaCl_2$/AA – water" has been studied as well, for the comparison. Moreover, the water and methanol sorption dynamics was investigated under typical conditions of AC cycle. Thus, the aims of this work have been (a) to optimize a texture of the AA layers; (b) to study the equilibrium and dynamics of water and methanol sorption on the composites based on $CaCl_2$ and LiCl inside pores of the selected AA layers; and (c) to evaluate feasibility of the new composites for AHT applications.

2. Materials and methods

2.1. The composite synthesis

The AA layers were synthesized by electrochemical oxidation of a flat aluminium plate (thickness 0.5 mm, surface area 5–16 cm^2, purity 99.999% Aldrich). The main components of an electrochemical rig (Fig.S1 in Supplementary materials) were: a power supply maintaining a constant current or constant voltage, digital voltmeter (±0.1 V), digital ammeter (±0.1 mA), carbon cathode, and aluminium anode. The latter is the aluminium sheet to be oxidized. The aluminium sheet was dipped into aqueous electrolyte solution, which was intensively stirred by a magnetic stirrer inside the temperature-controlled electrochemical cell (volume 170 or 500 cm^3). Three acids, namely sulphuric, oxalic and phosphoric, were used as electrolytes. One sheet side was protected from the oxidation by an acid resistant coat, so that anodization only took place from one face. The prepared AA/Al sandwiches were washed out with distilled water and dried at 160 °C. During the aluminium sheet oxidation, the main process characteristics (voltage, current, and temperature) were recorded by a data acquisition system. These characteristics were varied in a wide range to intently modify