

Aging study of carbon molecular sieve membranes

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Abstract

Further insight into the impact of air and humidity exposure on carbon molecular sieve membranes (CMSM) is provided. A CMSM was exposed to water vapor and to different dry environments (air, oxygen, nitrogen, propylene, etc.) for several months and the performance stability with time was analyzed periodically. In an effort to better understand the effect of oxygen on the fresh CMSM, regeneration at high temperature, used to remove some oxygen surface groups, was conducted 1 year after fabrication. The impact of oxygen removal from the surface on adsorption equilibrium, kinetic transport and pore structure is considered. Membrane aging as a result of oxygen adsorption was investigated on the heat-treated sample. This is the first time that oxygen chemisorption uptake rates have been measured on CMSM. Passivation methods and regeneration procedures on CMSM are also discussed.

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1. Introduction

Up to now, most authors have concentrated their efforts on the development of new strategies for producing carbon molecular sieve membranes (CMSM) in order to obtain improved gas separation performances, making most of the times basic characterization work. Little work has been done on studying some other important aspects related to these materials [1]. Although chemically and thermally resistant, CMSM present significant problems related to their performance stability. Comparing to carbon molecular sieve adsorbents (CMS) also used in gas separation application, CMSM permeation systems appears to be more vulnerable to oxidation, humidity and to blockage of the pore system [2,3]. A small change in the effective size of the pore constrictions can affect drastically the permeability toward an adsorbing gas molecule. Additional pore constrictions may be incorporated in the pore system by oxygen chemisorption and by strong adsorption of species presenting very low diffusivity. These species will block the pores and difficult the permeation of other ones. Furthermore, in spite of the low affinity of water on carbon surfaces, in the presence of hydrophilic groups and

at medium–high relative humidity, the presence of water can strongly reduce permeability toward other species. These aging-related issues, chemical adsorption, pore blockage and humidity, are further discussed below.

After the final heat treatment production step, CMSM present an amorphous nanoporous skeleton with a sharp pore size distribution (with critical size ranging from 0.3 to 0.7 nm). This structure is comprised of small and poorly aligned nanocrystallites. The nanocrystallites' faces are composed of graphene layers. Some nanocrystallite edges are terminated by thermally stable C–H groups and by some oxygen surface groups. Others are much more reactive, since they are terminated either by free radicals or by relatively stabilized π – σ electrons pairs [4]. These are commonly designated as active sites. The quantity and the nature of active sites on the carbon surface are dependent on the precursor and on the thermal history of the treatment [5]. When exposed to air, even at room temperature, oxygen atoms from air combine with some active sites forming oxygen surface groups. Thus oxygen chemisorption can eventually reduce the open porosity towards gas transport, offering additional restriction to diffusion, which is known as carbon aging.

Resulting from the close proximity of pore walls, sorption in micropores is enhanced due to higher interaction potentials. Taking part of that, carbon adsorbents are excellent for removing,

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from a process stream, strongly adsorbed compounds. However, for ultramicroporous membranes, this capacity may represent a problem. In CMSM application, the presence of large species or the inadvertent exposure to unsuspected contaminants can drastically reduce, either reversibly or irreversibly, the membrane performance. The ultramicropores can be easily obstructed by strongly adsorbed species with low diffusing rates that will progressively plug the pore system in relation to diffusion of other species. This plugging contaminant may coincide with the species that is meant to be purified. This was the case of the unsuccessful recovery of hydrogen from a concentrated hydrochloric acid gas stream using CMSM, in spite of the high ideal selectivities found [6].

Previous studies have shown that some degree of membrane performance is lost upon exposure to water vapor [7]. The vulnerability of CMSM to humidity is a complex phenomenon, considering the weak character of the water–carbon dispersion forces and the tendency of water molecules to form hydrogen bonds within the bulk phase. Water will initially adsorb onto hydrophilic sites, existing in the form of functional surface groups associated to non-carbon species. These sites are much more reactive than the atoms in the interior of the graphene sheets, and chemisorb foreign elements. Once the first water molecule is adsorbed, adsorbate–adsorbate interactions will promote the adsorption of further molecules through hydrogen bonds [8].

All the former effects have been reported in the literature, generally, through losses in membrane performances, that is, in most cases, these phenomena were not separately interpreted or quantified. Menendez and Fuertes [9] studied aging effects on membrane permeation, associated to air oxidation and humidity at room temperature. They reported that CMSM stored in dry or humid air underwent a rapid loss in permeance with time. CMSM stored under propylene and nitrogen was protected from damage. They suggested that oxygen chemisorption into carbon membranes instead of water physisorption is the main reason for the loss of permeance when a fresh carbon membrane is exposed to air. They supposed, however, that after several weeks the membranes tend to stabilize.

Jones and Koros [6,10] observed severe oxygen flux decreases when a CMSM was exposed to organic contaminants (hexane) concentrations as low as 0.1 ppm. Attempts to regenerate membranes after hydrocarbon exposure, using high temperature (363 K) in conjunction with vacuum were unsuccessful. The same authors [7] evaluated the performance of single-fiber test modules at various water activity levels (23–85% of relative humidity). The carbon membranes were adversely affected by exposure to water vapor. As the water activity level increased, membrane performance losses also increased. The water sorption data were not determined. They supposed that active sites, some at critical constrictions, were rapidly blocked by water molecules. They also proposed coating the membrane with a highly hydrophobic polymer (Teflon) [11]. This composite carbon membrane was significantly protected from humidity's adverse effects. Lagorsse et al. [8] studied water vapor adsorption equilibrium on CMSM and proposed a mechanism for water adsorption and desorption in nanoporous

carbons. Water adsorption isotherms displayed type V behavior and desorption hysteresis.

Passivation treatments have been studied to produce both highly hydrophobic and stable surfaces, specially in the field of activated carbon materials [12]. These methods intend to prevent further oxygen sorption at ambient temperature and reduce the affinity of the porous structure to water adsorption. Several authors [12,13] stated that high-temperature treatment in an inert environment is effective in removing oxygen-containing surface groups from activated carbons, but leaves a surface containing very reactive carbon sites capable of quickly re-adsorbing oxygen at room temperature. They stated that hydrogen treatments are preferred in the sense that an increasingly stable surface is obtained. Treatment in H₂ not only removes oxygen (in the form of CO and CO₂) but also removes some of the very reactive residual carbon atoms (as CH₄). Furthermore, Menendez et al. [14] showed that the stability achieved is not due only to the elimination of the most active sites, but is also a consequence of the modification of the nature of the active sites, which, after the passivation, only re-adsorb oxygen at elevated temperatures.

The main objective of this paper is to better understand the effect of the CMSM exposure to air and humidity. The surface chemisorption of oxygen, one of the most important aging agents, is studied for the first time in these materials. Its effect on the adsorption equilibrium and on the diffusivity towards various species is analyzed and it is suggested how the oxygen-induced aging affects the pore structure of the membranes. To accomplish that, a CMSM was stored in different chemical environments during several months and its performance was systematically checked. One year after its fabrication, the membranes were treated for removal of surface functional groups and passivation, reproducing the last step of the CMSM production. This treatment may be used to restore the fresh permeation membrane properties. Passivation methods and regeneration procedures are discussed.

2. Experimental

The carbon molecular sieve membranes (CMSM) characterized and tested in this study were supplied by Carbon Membranes Ltd. in Israel and were designated as samples MS. The production steps involve pyrolysis followed by chemical vapor deposition (CVD) and an activation step, which consists on a high temperature oxygen treatment. This process was described elsewhere [1]. Samples MS consist of carbon molecular sieve hollow fibers, having a uniform wall thickness of 9 μm and an external diameter of 170 μm.

The performance of MS stored in different chemical environment during several months was evaluated doing single gas permeation measurements in a dead end permeation module, in a temperature-controlled system. The membrane module used, containing a bundle of 95 fibers, was designated as MS module. The experimental set-up and the construction of the hollow fiber membrane module were described elsewhere [1].

The partial removal of oxygen surface groups from MS was achieved by heating a sample in a reducing atmosphere. This treatment mimics the final production step used by the com-

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