



Network model for the evolution of the pore structure of silicon-carbide membranes during their fabrication

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ABSTRACT

A pore-network model is developed to study the evolution of the pore space of a nanoporous silicon-carbide membrane during its fabrication by the chemical-vapor infiltration/chemical-vapor deposition (CVI/CVD) techniques. The pore space of the support is represented by a three-dimensional network of interconnected pores, in which the pores' effective size is distributed according to a pore size distribution (PSD) that closely mimics the experimental PSD. The chemical reaction that generates the SiC, the various transport mechanisms in the pores, and the evolution of the pore structure during the SiC deposition on the pores' surface are included in the model. The Maxwell–Stefan equations are used for describing the pore-level transport processes, which include the Knudsen and hindered diffusion, as well as viscous flow. The effect of pore shrinkage and blockage as a result of the deposition of the SiC on the pores' internal surface is taken into account. The simulator monitors the PSD as the membrane's structure develops by the CVD process and evolves. Also computed are the permeances of argon, the carrier gas, and of helium during the CVD, as well as the membrane's selectivity. Good agreement is found between the simulation results and the experimental data. Thus, the model may be used for determining the optimal conditions under which a membrane may achieve a given value of permselectivity.

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1. Introduction

Silicon carbide (SiC) has many unique and desirable properties, which have made it a prime candidate for fabrication of nanoporous membranes [1–7]. Being permselective at high temperatures, particularly in the presence of steam, has made the SiC membranes an excellent candidate for applications in membrane reactors. Indeed, in the water–gas shift and methane steam-reforming reactions, where the membrane must function in the presence of high-temperature steam, the performance of the SiC membranes has been shown to be promising [1–4]. There are several ways to fabricate the membranes, such as the sol–gel technique, pyrolysis [2–4], and chemical-vapor infiltration (CVI)/chemical-vapor deposition (CVD) [2,8–10]. It is the last technique that is of interest to us in the present paper.

The CVD is widely used in the chemical and semiconductor industries. The evolution of the pores' size, the transport of the reactants through the pore space, and determination of the kinetics of the CVD reaction are of much current research interest [11–15]. To develop deep understanding of the CVD process, one must have an accurate model of the pore space in which the CVD process takes

place, as well as the correct mechanism(s) by which molecules and their mixtures are transported through the pore space. If such a model is developed, it may be used for optimizing the performance of the membranes.

Since the CVD/CVI processes involve the transport of the reactants in a pore space, various approaches have been used to model such transport processes in porous materials. One approach is based on the classical equations of transport [11–13,16,17]. For example, Langhoff and Schnak [17] modeled the CVI of pyrolytic carbon as a moving boundary problem, in order to determine the evolution of the structure of the pyrolytic carbon layer, using a one-dimensional continuum model. Such an approach can neither take into account the effect of the morphology of the pore space, i.e., its pore size distribution (PSD) and pore interconnectivity, on the transport of the gases, nor can it be predictive quantitatively, unless several adjustable parameters are introduced into the model.

A realistic approach is one that represents the porous material by a network of interconnected pores (or bonds), joined together at the network's nodes [18–21]. Since most porous materials contain interconnected pores, the connectivity affects the transport of gases through their pore space. In addition, a fraction of the pores may be plugged as a result of the deposition of the reaction products on their surface and become inaccessible to the reactants during the deposition part of the CVD/CVI. If the fraction of the inaccessible pores reaches the percolation threshold of the pore space [22–25],

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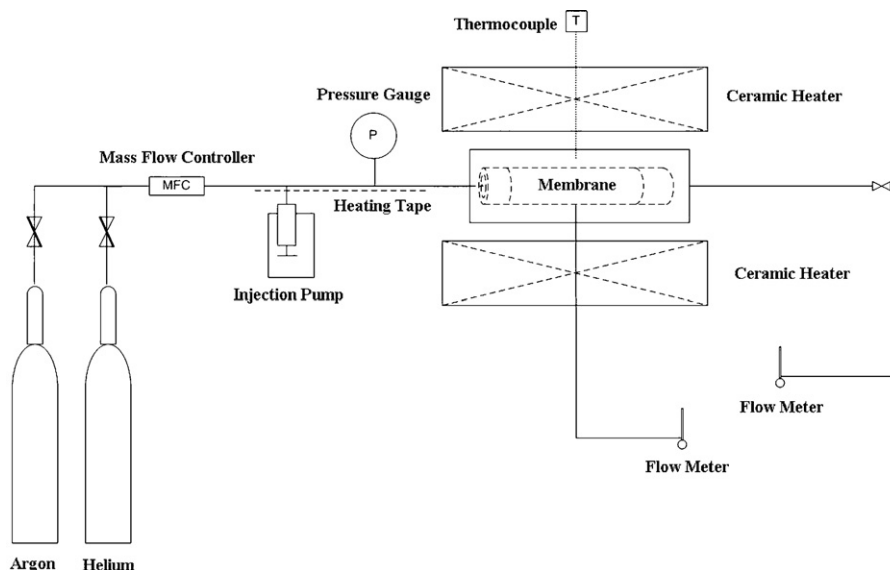


Fig. 1. Schematic of the apparatus used for the preparation of SiC membrane.

the porous medium will lose its global connectivity and macroscopic transport of the gases ceases. The percolation threshold is the minimum fraction of the unplugged pores for the formation of a sample-spanning cluster of open pores.

The shrinkage of the pores and their blockage also occur in a variety of other important phenomena and, therefore, have been studied using pore-network models. Sahimi and Tsotsis [26] and Arbabi and Sahimi [27,28] studied the pore blockage phenomenon in the deactivation of porous catalysts. Nukunya et al. [29] studied the clogging of the pore space due to the biomass growth from the biodegradation of organic compounds. Wood et al. [30] developed a pore-network model that incorporated a model of diffusion and reaction in the pores and the analysis of the pore-filling sequence by capillary condensation. Their model was general, allowing for any type of kinetic expression for the reactions. Beigi et al. [31] utilized the pore-network model to study catalytic dehydration of methanol.

In the present paper we develop a pore-network model for the evolution of the pore space of nanoporous SiC membranes during the CVI/CVD processes that we have been studying experimentally, and investigate the transport and reaction of a binary mixture of a polymeric precursor A (tri-isopropylsilane, or TPS) and the carrier gas B (argon, Ar) in the pore space. The results of the computer simulations are then compared with our own experimental data. To our knowledge this is the first time that such a model has been developed for the evolution of a membrane's pore space during the CVD and/or CVI processes.

The rest of this paper is organized as follows. We first briefly describe the experimental procedure for the fabrication of the SiC membrane. The formulation of the pore-network model and its details are then described. Next, we describe the numerical and computer simulation methods that are used. The results are then presented and discussed. The paper is summarized in the last section.

2. Experimental procedure

In order to fabricate the SiC membrane, we utilized a SiC tubular support with inside and outside diameters, respectively, of 1/4 and 1/2 in. The tube's length was in the range 1.5–2.5 in, while its average pore size was 65 nm (determined experimentally by permoporometry; see below). The support was prepared in our lab-

oratory using a tubular pressing mold and the HSC059 SiC (0.6 μm particle size) powder, as previously described [1,8].

Prior to being utilized for the membrane fabrication, the supports were treated in flowing air at 450 °C, in order to remove any excess carbon that may be present. We used the TPS (purchased from the Aldrich Company) as the polymeric source of silicon, and an ultra-high purity Ar (the purity was 99.999%) as the carrier gas, with its flow rate varying from 0.5 to 10 ml/s. The hot-wall CVD reactor is made of stainless steel Swagelok fittings, together with a cross-union. One outlet of the cross-union was used as the permeate side, one to insert the thermocouple, while the remaining two were used as the inlet and outlet for the CVD reactor. A ceramic cylindrical heater was used to heat up the reactor, controlled by an Omega temperature controller (CN 9000). A syringe pump (Harvard PHD2000) was used to inject the TPS precursor into the carrier gas at a pre-determined rate. The feed lines from the pump to the furnace were heat-traced and kept at 140 °C at all the times, in order to ensure that the TPS remained in the vapor phase. The injection rate of the TPS was varied from 5 to 20 $\mu\text{l/h}$, while the reactor pressure was varied from 1 to 25 psig. The temperature was adjusted in the range 760–800 °C during the deposition. The schematic of the apparatus is shown in Fig. 1.

The membrane's permeation characteristics were measured online during the CVD/CVI deposition process. The permeance of, for example, Ar in the temperature range 760–800 °C prior to the deposition was 5.8×10^{-8} mol/Pa s m^2 , and decreased to about 8×10^{-9} mol/Pa s m^2 . Fig. 2 presents the typical results obtained with one of the SiC support tubes with an initial porosity of $\epsilon_0 = 0.3$ prior to the deposition. In these experiments the deposition pressure P_{in} in the reactor was ~ 1.2 atm, while the pressure P_{out} in the inner tube was held at ~ 1 atm.

The permeances of Ar and He, measured in-situ during the CVI/CVD deposition experiments, are compared in Fig. 2. During the first 39 h the permeance of both gases decreases as the deposition proceeds. However, relatively speaking, the He permeance decreases more slowly than that of Ar. This behavior may be explained by observing that at the beginning of the experiment the disk is mesoporous, and both Ar and He are transported by the Knudsen diffusion. As the TPS decomposes into SiC (and other reaction products) and gradually fills up the membrane's pores, the average pore size decreases, hence decreasing the permeance of both gases. But, with He being the smaller of the two molecules,

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