V.N.9 Nanoporous Membranes for Hydrogen Production: Experimental Studies and Molecular Simulations

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Abstract

In this project, we study SiC nanoporous membranes, which exhibit the potential to overcome many of the difficulties other inorganic membranes face, particularly under conditions typically encountered in reactive separations for H_2 production, and in fuel-cell applications. In particular, we systematically investigate and further develop the technique of pre-ceramic polymer pyrolysis to produce nanoporous SiC membranes and films, which are both cost-efficient and industrially viable. Our efforts are motivated by the growing interest in the H_2 economy, which necessitates the development of robust nanoporous materials for use in high-temperature and pressure processes related to H_2 production. SiC is a promising material for such applications, due to its many unique properties, such as high thermal conductivity, thermal shock resistance, chemical inertness and high mechanical strength. The main focus of our project is on trying to understand the formation process of the membranes, namely, how the initial structure of the polymeric precursor and the pyrolysis conditions impact the final membrane characteristics. Our efforts involve extensive experimental investigation of the membrane formation process, as well as modeling of the pyrolysis process itself by molecular dynamics simulations, since the understanding must be at the molecular level. The new science that is being developed impacts not only the fabrication of SiC membranes, but also the general field of inorganic membranes, including carbon molecular-sieve (CMS) and mixed-matrix membranes. A key outcome of our effort will be the ability to prepare a membrane with certain "optimal" properties (e.g., permeance, separation factor, and surface characteristics) by being able to determine in a systematic way the type of polymeric precursor one needs to use, and the preparation method and procedure that one must utilize.

Progress Report

The results of the work accomplished in this project are summarized as follows:

Highly permeable macroporous SiC supports have been prepared. In our efforts we have investigated a variety of factors that impact the properties of these supports. They include, (i) the type and composition of the starting powders utilized; (ii) the type and quantity of sintering aids and the temperature and other conditions of sintering, and (iii) the impacts of various surface treatments. A novel dip-coating technique has been developed that involves modification of the slip-casting step using SiC nanofibers and nanotubes, which provides a more effective means for preventing infiltration in the underlying macroporous structure during both the slip-casting and the subsequent thin film deposition steps. Using this preparation technique, membranes have been prepared with very high (He/Ar) separation factors of more than 2000, while using substrates with significantly higher surface roughness. MD simulations were employed in order to examine the adsorption and diffusion of N_2, H_2, CO_2, CH_4, and n-C_4H_{10} in silicon carbide nanotubes (SiCNT's). The simulations indicated the strong effect of the nanotubes' chirality and curvature on the pressure-dependence of the adsorption isotherms and the self-diffusivities. Detailed comparison was made between the results and those for the CNT's, and the hydrogen adsorption capacity of the SiCNTs is higher than the CNTs' under the conditions that we have studied. A templating technique has also been developed for the preparation of high-surface area SiC materials with highly-interconnected pore structures. These materials, in addition to finding useful applications as membrane films, also show potential to find important applications as adsorbents, catalyst supports and energy storage media (e.g., supercapacitors).

In order to gain insight into the processes that prepare these nanoporous materials, we have developed a class of models, referred to as the *geometric models*, which aim to understand the effect of the material's morphology, such as its pore-size distribution (PSD) and pore interconnectivity, on its sorption and transport characteristics, and on its ability to separate molecular mixtures. These models make use of an annealing method to generate the solid matrix of the SiC material via the semi-empirical, extended Brenner force

field (FF), previously utilized to model various phenomena involving SiC bulk materials and surfaces by MD and MC simulations. The method consists of starting in the crystalline β-SiC state, raising the temperature until the crystal melts, and then decreasing the temperature gradually to the desired value. The material's pore structure is generated via a Voronoi space tessellation technique, which creates a 3-D pore network within the resulting material. Its characteristics (porosity, PSD, interconnectivity) are fine-tuned by fitting, via atomistic (GCMC) simulations, experimental single-gas (e.g., N_2 and CO_2) adsorption data. The resulting model membrane structures are then used to study the transport of single gases and binary gas mixtures. Due to the nano-scale size of the membrane pores, it is of paramount importance to understand the interactions between the molecules and the pore walls and their influence on the transport processes, as they determine the ability of the SiC materials to separate mixtures based on differences in molecular mobility. To accomplish that, we utilize non-equilibrium molecular dynamics (NEMD) simulations, and for certain gas pairs the results agree qualitatively with our experimental data.

Despite their modest success in matching experimental transport and separation data, the geometric models offer little in terms of predictive capabilities, as they do not use information about the chemical structure of the polymeric precursors and the membrane's preparation method. For modeling to be predictive, an accurate, detailed knowledge of the pore space, and a molecular-level understanding of the pore surfaces are of paramount importance. In addition, one must accurately mimic the processes that are involved in the fabrication of the membranes. This then requires the development of a reactive FF that correctly models the pyrolysis process that generates these materials. In our current efforts, we have begun to expand and to further improve the ReaxFF for PDMS, originally proposed by Professor William Goddard and his team at Caltech, who collaborate with us in our current efforts, and will adopt it for the investigation of the pyrolysis of allylhydridopolycarbosilane (AHPCS) at high temperatures. In our simulations so far we have focused attention on hydridopolycarbosilane (HPCS) as it prepares, in principle, a ceramic with a stoichiometric Si:C ratio. Experimentally, on the other hand, we have found during our present efforts that AHPCS provides better experimental flexibility in preparing SiC membranes. During the renewal period, therefore, we will extend our efforts to also simulate AHPCS pyrolysis. As a first step towards simulating the pyrolysis process of the pre-ceramic precursor that forms the SiC, we generate a realistic model of the polymer itself utilizing energy minimization and MD simulations and the polymer-consistent FF (PCFF). The figure below shows a HPCS amorphous polymer originally built by introducing four polymer chains, each having 482 atoms, in a periodic cell box of 28.9 Å in size using the modified self-avoid walk (SAW) method.

Our reactive (RMD) simulations using ReaxFF (below the SiC melting point) yield the initial pyrolysis products of the HPCS to be hydrogen and associated polymer fragments, indicating that decomposition and subsequent cross-linking of the polymer are initiated by Si-H and C-H bond cleavage. Secondary reactions (involving produced radicals) lead to cross-linking between Si and C atoms of adjacent chains, yielding eventually the formation of the amorphous SiC structure. We have studied the temperature-dependence of the HPCS pyrolysis by following the rate of production of the H radicals using reactive molecular dynamics (RMD) simulations with ReaxFF. We have also tracked the temperature dependence of the H radical production in order to extract the Arrhenius parameters for the failure modes of the HPCS. Further, we have validated the ability of ReaxFF to represent the equation of state of the SiC crystal by testing against its more than 250 crystalline structures, and its three major known polytypes.

The structure of SiC is generated by carrying out extensive RMD simulations in the NVT ensemble in the temperature range (2000 - 3000 K). During the simulations, the hydrogen radicals (key product of the pyrolysis process) are removed from the simulation box as a way of speeding up the simulations, and the structure is cooled down to 2000 K. Then, MD simulations in the NPT ensemble are utilized to compress the system at 2000 K. Eventually the system is relaxed at ambient temperature to arrive at the amorphous structure of SiC. To test the validity of the model, in addition to calculating the entropy and radial distribution function, we also computed the melting point, the X-ray diffraction (XRD) spectra, and other structural properties. In order to assess the ability of the ReaxFF simulations to be predictive, model validation via comparison with experiments is of critical importance, and will be a key focus of the proposed efforts in the future. Figure 2 presents a comparison between the computed radial distribution function and the experimental data.
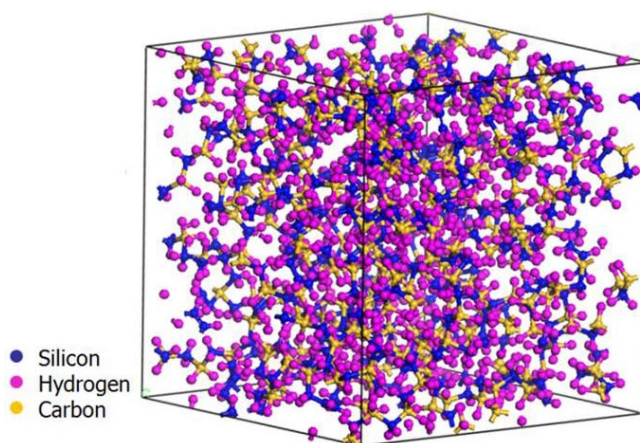

● Silicon
● Hydrogen
● Carbon

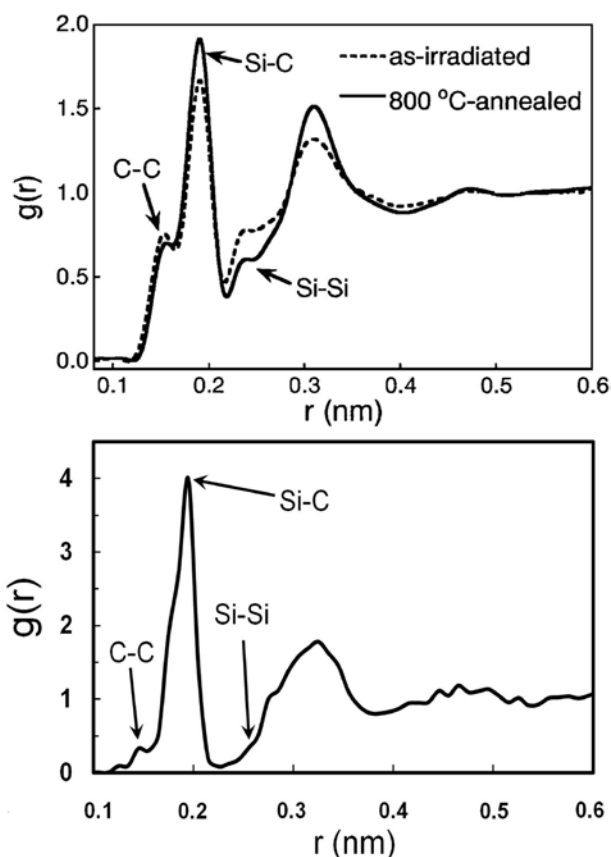**FIGURE 1.** HPCS amorphous polymer structure

FIGURE 2. Comparison of the computed radial distribution function of the amorphous SiC (below) with the experimental data (top).

In an attempt to model the formation process of the membranes at a coarse scale, a pore network model has also been developed to study the evolution of the pore space of a nanoporous SiC membrane during its fabrication by (CVI/CVD) techniques. Good agreement was found between the simulation results and the experimental data. Thus, the model may be used, in conjunction with the molecular-scale model, for determining the optimal conditions under which a membrane may achieve a given value of permselectivity.

A network model was also developed to interpret the results of flow permporometry (FPP) that has been used widely for determining the pore size distribution of a broad

class of porous materials, including our studies of the high-flux macroporous SiC supports. The model is the first of its kind, even though permporometry has been used for decades.

We have also begun to study other nanostructures, including SiC nanotubes, as a potential material for storage of hydrogen, as well as separation materials and sensors. So far, we have studied adsorption and diffusion of a variety of gases in SiC, both experimentally and by MD simulations. We have also measured adsorption of nitrogen in carbon nanotubes, in order to compare the data with those measured with SiC nanotubes. The preliminary results have been very encouraging.

Publication list (including patents) acknowledging the DOE grant

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