SiC-Based Hydrogen Selective Membranes for Water-Gas-Shift Reaction

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ABSTRACT

This technical report summarizes our activities conducted in Yr II. In Yr I we successfully demonstrated the feasibility of preparing the hydrogen selective SiC membrane with a chemical vapor deposition (CVD) technique. In addition, a SiC macroporous membrane was fabricated as a substrate candidate for the proposed SiC membrane. In Yr II we have focused on the development of a microporous SiC membrane as an intermediate layer between the substrate and the final membrane layer prepared from CVD. Powders and supported thin silicon carbide films (membranes) were prepared by a sol-gel technique using silica sol precursors as the source of silicon, and phenolic resin as the source of carbon. The powders and films were prepared by the carbothermal reduction reaction between the silica and the carbon source. The XRD analysis indicates that the powders and films consist of SiC, while the surface area measurement indicates that they contain micropores. SEM and AFM studies of the same films also validate this observation. The powders and membranes were also stable under different corrosive and harsh environments. The effects of these different treatments on the internal surface area, pore size distribution, and transport properties, were studied for both the powders and the membranes using the aforementioned techniques and XPS. Finally the SiC membrane materials are shown to have satisfactory hydrothermal stability for the proposed application. In Yr III, we will focus on the demonstration of the potential benefit using the SiC membrane developed from Yr I and II for the water-gas-shift (WGS) reaction.

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TECHNICAL SUMMARY

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Powders and supported thin silicon carbide films (membranes) were prepared by a sol-gel technique using silica sol precursors as the source of silicon, and phenolic resin as the source of carbon. The powders and films were prepared by the carbothermal reduction reaction between the silica and the carbon source, which was conducted at 1550 ^{o}C under an inert atmosphere of argon. The powders and films were characterized by XRD, and BET for their surface area and pore size distribution. The SiC membranes were also characterized by permeation tests using single gases (He and Ar) to determine their separation characteristics. The XRD analysis indicates that the powders and films consist of SiC, while BET shows that they contain micropores. SEM and AFM studies of the same films also validate this observation. The powders and membranes were also subjected to treatment at different corrosive and harsh environments, including immersing them in HF, burning in air, and reacting with steam at high temperatures. The effects of these different treatments on the internal surface area, pore size distribution, and transport properties, were studied for both the powders and the membranes using the aforementioned techniques and XPS. The materials are shown to have satisfactory hydrothermal stability.

In Yr III, we will focus on the demonstration of the potential benefit using the SiC membrane developed from Yr I and II for the water-gas-shift (WGS) reaction.

1. INTRODUCTION

Sol-gel processing techniques are receiving attention recently in the preparation of ceramic membranes.[1-5] Ceramic membranes are better suited than the conventional polymeric membranes for high temperature separation applications, due to their good resistance to high temperatures.[6-7] Silicon carbide (SiC) is a particularly promising material for the preparation of high temperature membranes, since it is capable of withstanding high temperatures and mechanical stresses, and it is resistant to highly corrosive environments.

Relatively few studies have reported on the preparation of SiC membranes by any techniques.[8,9] Morooka, *et al.* [8] prepared SiC membranes by chemical vapor deposition on γ-alumina substrates at 700-800 ^{o}C using tri-isopropylsilane as the precursor. After the deposition process, the membranes are heat-treated in argon at 1000 ^{o}C for 1 h. The resulting membranes are tested for the separation of H_2/H_2O mixtures. The permeation experiments are performed at temperatures between 200 ^{o}C and 400 ^{o}C, and have shown a H_2/H_2O selectivity in the range of 3-5.[8] SiC membranes were prepared by chemical vapor infiltration (CVI) into γ-Al_2O_3-coated porous α-Al_2O_3 tubes by Takeda *et al.*[9] The gases utilized were SiH_2Cl_2 and C_2H_2 diluted with hydrogen. They were supplied alternatively to the porous tube during heating at 800-900 ^{o}C. The produced SiC membrane showed hydrogen permeances in the range of $1x10^{-8}$ $mol.m^{-2}.s^{-1}.Pa^{-1}$ with a H_2/N_2 selectivity of 3.36 at 350 ^{o}C. Using γ-alumina as the support for the preparation of silicon carbide membranes presents a number of challenges for the type of applications these membranes may be useful for. Porous γ-alumina is not very resistant to corrosive environments. In addition, its thermal expansion coefficient is different from that of silicon carbide, raising concerns about the mechanical stability of the resulting composite membrane system. Lee and Tsai [10] have prepared asymmetric SiC membranes by low-pressure chemical vapor deposition (LPCVD) of SiH_4, C_2H_2 and argon mixtures at 800 ^{o}C on the surface of Al_2O_3-doped SiC macroporous supports. The macroporous SiC support, itself, had an asymmetric structure, i.e., the alumina content decreased from the center to the surface of the support. The CVD process reduced the pore size of the membrane from 297 nm to 14 nm.[10] However, this pore size reduction is achieved at the cost of a large reduction in the permeance of the membranes. Part of our Yr II effort has devoted to the preparation of SiC mesoporous and macroporous substrates for use as supports in the preparation of asymmetric SiC membranes. We have used a number of different starting powders and sintering aids to prepare

crack-free substrates, which have high porosity and are sufficiently smooth, to be used for further processing by sol-gel, CVD and other techniques. Our study was reported in a recent publication by Suwanmethanond *et al.* [11]

In this annual report we describe the results of our investigations on the use of these substrates for the preparation of asymmetric SiC membranes using a sol-gel method. In our study we have utilized a number of commercial silica sols with different sol particle sizes. These are used as the silicon source for production of SiC. Phenolic resin is utilized as the carbon source. The SiC sol precursors are then coated on the SiC substrates, which are prepared by our group [11] using dry-pressing techniques, and sintering at 1950 ^{o}C. The SiC sol precursors undergo carbothermal reduction at high temperatures to produce the final SiC thin films. The sol-gel step is an important intermediate stage in the preparation of asymmetric microporous SiC membranes (the final stage can be a CVD/CVI or a polymeric precursor pyrolysis step), which are capable of withstanding high service temperatures and are thermally stable to the presence of steam. These sol-gel membranes, in addition, can potentially find application in nano- and ultrafiltration applications of corrosive liquid mixtures.

We are not aware of other studies, which report on the use of a sol-gel technique for the preparation of SiC membranes. A number of prior studies in recent years have, however, focused on the preparation of SiC powders using sol-gel techniques. Cerovic *et al.,* [12] for example, have prepared silicon carbide powders by heating a mixture of a silica sol, prepared by an ion exchange method, with saccharose or activated carbon (as the carbon sources), and boric acid; the latter is reported to act as the catalyst for the carbothermal reduction of silica with carbon at 1550 ^{o}C. They report that the optimum molar ratio of C/Si for the production of SiC is 3 for activated carbon and 4 for saccharose. The diameter of the spherical SiC particles prepared with activated carbon was twice that of the particles prepared from saccharose. Using phenyltrimethoxysilane (PTMS), and/or tetraethylorthosilicate (TEOS) as the silica source Seog and Kim [13] have prepared silicon carbide powders, which are made of spherical particles. Mono-dispersed spherical powders were produced using a base catalyzed route, while poly-dispersed powders were obtained with the aid of an acid-base catalyzed route. A number of different carbon sources such as ethycellulose, polyacrylonitrile (PAN), and starch were utilized by Raman *et al.* [14] for reaction with a silicon source at 1550 ^{o}C to produce SiC powders. It was shown that the type of carbon source utilized determines the crystalline form of SiC that is produced and the grain size.

As noted previously, there are no published studies, we are aware of, that specifically focus on preparing SiC membranes using a sol-gel technique. The preparation of such membranes presents unique challenges, since the thin gel film that is generated on the porous substrate, typically using a dip-coating method, must remain crack-free during the SiC forming process at high temperatures.

2. EXPERIMENTAL PROCEDURE

2.1. The Sol-gel Synthesis of Silicon Carbide

A variety of silica sols (both water and alcohol based) have been utilized in the investigation. For the materials, whose preparation is described here, a particular organo-silica sol type IPAST, with a particle size in the range of 8-10 nm (see Fig. 1) is used as the silica source, as received from the manufacturer (Nissan Chemical Industries, Ltd). A phenolic resole type resin (Occidental Chemical) is used as the carbon source. A 50 wt % solution of phenolic resin in ethanol is mixed with the silica sol in a quantity that is adjusted to obtain a molar ratio of Si/C =1:3. The choice of this Si/C molar ratio is based on the stochiometric requirement for the completion of the overall carbothermal reduction reaction, which is thought to proceed as follows: [15]

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad\qquad (1)$$

The mixture of silica sol and phenolic resin is then sonicated using an ultrasonic device for 10 min in order to obtain a homogeneous gel-polymer mixture. Subsequently, the procedure one follows depends on whether one prepares powders or membranes. For the powders, the sample is dried at room temperature overnight and then transferred into an alumina crucible. The crucible containing the dried gel is then placed in a tubular furnace. The samples are heated first up to 800 ^{o}C with a heating rate of 75 ^{o}C/h and then up to 1550 ^{o}C with a heating rate of 50°C/h. The gel is calcined at 1550 ^{o}C for 3 h; upon calcination it is then cooled down to room temperature at a rate of 85 ^{o}C/h. During the calcination process the sample is constantly purged with ultra-high purity argon. The membrane preparation is described below.

2.2. Membrane Preparation Using the Sol-Gel Method

The supported SiC sol-gel membranes are prepared utilizing macroporous SiC substrates. These substrates are prepared as follows.[11] A silicon carbide fine powder (Sumitomo Osaka Cements, Japan) with an average particle size of 0.03μ is mixed with a more course silicon carbide powder (Superior Graphite Co.,) with an average particle size of 0.6μ in the ratio of 1:2. Boron carbide (in the amount of 0.1 wt %) and phenolic resin (in the amount 4 wt %) are used as the sintering aids. The mixture of powders and various sintering aids are pressed into disks, which are then calcined at 1950 °C to obtain the macroporous SiC membrane substrates (more details about the preparation of such substrates can be found in our prior publication).[11] These SiC substrates are then used for further surface modification via the sol-gel technique.

The silicon carbide membranes are prepared by conventional dip-coating techniques. One first prepares the solution containing the appropriate amounts of the silica and carbon sources and sonicates it for 10 min in order to obtain a homogeneous blend. The macroporous SiC substrate to be dip-coated is wrapped with Teflon tape on one side, and is dipped in the sol solution for a period 30 s; it is then withdrawn out of the solution with a withdrawal rate of 0.001m/s. After the coating process is completed, the coated substrate disk is placed in an alumina crucible and is then inserted in the tubular furnace. The sample is heated to 1550 °C with a heating rate of 50 °C/h, where it is calcined for 3 h under an argon atmosphere; upon calcination it is cooled to room temperature with a cooling rate of 50 °C/h. If additional coatings are required they are applied after the first calcination step using the same dip-coating/calcination procedure.

2.3. The Characterization of SiC Membranes

The permeation characteristics of the membrane are measured using argon and helium as the test gases. The transport properties of each membrane are reported in terms of the permeance of the two individual gases and the ideal separation factor (defined as the ratio of permeances of these two gases). The absolute values of permeance and the separation factor are both important in terms of determining the usefulness of the membrane for further applications and processing. The permeance of each species is measured using a laboratory permeation apparatus, which has been described elsewhere.[11] Briefly the membrane disk is placed in between the two half-cells of the apparatus, one chamber is pressurized at the required pressure, while the other is maintained at atmospheric pressures. The flow rate of gas exiting the lower pressure chamber Q_i (m^3/s) is measured using a soap-bubble flow meter. Since the thickness of the

thin layer is not precisely known the permeance (instead of the permeability) of each gas K_i in $m^3/(m^2 \, Pa \, s)$ is calculated from the following equation.

$$K_i = Q_i/(A \Delta P_i),\qquad\qquad(2)$$

where A is the cross-sectional area (m^2), and ΔP_i is the pressure difference that exists across the membrane disk (Pa). The separation factor between He and Ar, as noted previously, is defined as the ratio of their permeances calculated from equation (2). If the sol-gel membrane has no substantial number of macroporous defects being present, one expects this ratio to be equal to the Knudsen separation factor (S_k) given (for the case of the He and Ar pairs) by the following relationship.

$$S_k = \sqrt{\frac{MW_{Ar}}{MW_{He}}}\qquad\qquad(3)$$

where the MW_i's are the molecular weights of the two permeating gases.

For both the powders and the membranes X-ray diffraction (XRD) analysis is used in order to identify the crystalline compounds that are present. The XRD technique is complemented with X-ray photoelectron spectroscopy (XPS) measurements, which determine the surface composition of the materials. XPS can potentially identify amorphous compounds, which may not be detected by XRD. The pore size distributions of both powders and films are measured using an ASAP2010 (Micromeritics) BET apparatus. For BET data analysis we utilize the BJH and Horvath-Kawazoe models. Therefore, the pore size distributions (PSD) generated must only be viewed as qualitative measures of the pore structure (two SiC membranes with the same PSD's are likely to have the same pore structure characteristics) rather than as quantitative indicators of the pore size. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are also used to study the surface morphology of the membranes. The SEM technique is used to locate the position of the film, and in order to determine the degree of its adhesion to the underlying macroporous substrate. AFM is utilized to determine the degree of surface roughness, which is important when determining whether these materials are appropriate as substrates for the further deposition of microporous films by other techniques.
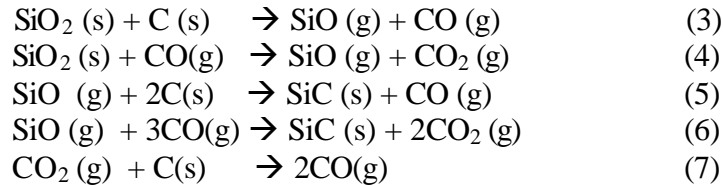
The hydrothermal stability of the powders and the membranes is tested by treating them at 350 ^{o}C in flowing ultra high purity argon containing 50% mole of steam for a pre-determined period of time. Upon completion of the hydrothermal

tests the powders and membranes are tested again by a variety of techniques in order to determine the effect of the treatment on surface and transport properties.

3. RESULTS AND DISCUSSION

3.1. The SiC Powders

Sol-gel production of silicon carbide involves the reaction between silica and a carbon source at relatively high temperatures. This calcination formation process is also called the carbothermal reduction reaction. This is because during the process silica is reduced (loses its oxygens) by a series of reactions, and is eventually converted to silicon carbide. The carbothermal reaction and the formation of silicon carbide can be easily traced using X-ray diffraction analysis. The bottom line in Fig. 2, for example, shows the XRD pattern of a silicon carbide powder prepared by us by the sol-gel method previously described and after the calcination process. The XRD pattern indicates that the carbothermal reduction reaction has resulted in a material, which is pure silicon carbide, its peaks corresponding to that of crystalline β-SiC. The following set of reactions have been reported to occur during the carbothermal reduction reaction:[16, 17]

$$SiO_2\ (s) + C\ (s) \rightarrow SiO\ (g) + CO\ (g) \qquad (3)$$
$$SiO_2\ (s) + CO(g) \rightarrow SiO\ (g) + CO_2\ (g) \qquad (4)$$
$$SiO\ (g) + 2C(s) \rightarrow SiC\ (s) + CO\ (g) \qquad (5)$$
$$SiO\ (g) + 3CO(g) \rightarrow SiC\ (s) + 2CO_2\ (g) \qquad (6)$$
$$CO_2\ (g) + C(s) \rightarrow 2CO(g) \qquad (7)$$

Here (s) and (g) refer to solid and gaseous states, respectively. The main reactions for the formation of SiC are reactions (3) and (5). Reaction (3) occurs rapidly at high temperatures; the SiO(g) that is produced reacts with C(s) that is in close proximity and forms SiC(s). When enough CO and CO_2 are present reactions (4), (6), and (7) may also occur. It is clear from the above mechanism that the miscibility of the carbon source (e.g., the phenolic resin solution) with the silica sol plays an important role in the formation of the final SiC microstructure. The silica sol and phenolic resin need to be homogeneously and well mixed with each other in order for the SiO_2 and C to be in intimate contact and for crystalline SiC to be produced.

Though β-SiC appears to be the form of SiC that forms immediately after the carbothermal reaction treatment of such powders under various conditions

may convert this form of SiC into other forms. As can be seen in Fig. 2 treatment of the powder in flowing air at 420 ^{o}C for 3 h leaves the β-SiC phase unchanged. Treatment in a strong hydrofluoric acid (HF) solution (Aldrich, 40 wt% HF) for 5 h also seems to have a minor effect on the SiC powders. Treatment in a flowing mixture of 50-mol% water and 50-mol% argon at 350 ^{o}C for 24 h (after it had been treated in air at 420 ^{o}C for 3 h) seems to convert part of the β-SiC into α-SiC (see top of Fig. 2). Bootsman *et al.*[18] have studied the phase transformation of different SiC phases. They concluded, in agreement with our own observations, that the 6H (α-SiC) type is generally the most stable phase. However, whether the other crystal polytypes (including β-SiC) convert into α-SiC depends on the type and pressure of the atmosphere that prevails, and the type and amount of dopants and impurities that are present in the sample.

To understand the nature of the materials that are formed by the sol-gel technique, and in order to evaluate their performance in corrosive and oxidative environments the as prepared powder samples were subjected to further tests. Three different types of treatments were applied in various sequences (see Table 1). They include heating of the silicon carbide samples in air at 420°C for varying periods of time (as indicated in Table 1) in order to burn away any unreacted carbon; washing in a strong HF solution (Aldrich, 40 wt% HF), which has been reported by other investigators to etch away any residual silica that may be left behind from the carbothermal reduction reaction;[19] and subjecting the samples to a treatment at 350 ^{o}C in flowing ultra high purity argon containing 50% mole of steam for a pre-determined period of time, a hydrothermal stability test which is important in terms of the eventual application of such membranes. Table 1 shows a number of different sequences of tests performed on the sol-gel SiC samples in order to study the effect of each step individually and in combination. We have taken the internal surface area of the powder samples (as measured by BET) as an indicator of the changes in the pore structure brought upon by the various treatments.

Table 1. The surface area of SiC samples after undergoing various treatments.

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                        ┌─────────────────────┐
                        │      sol + C        │
                        │  calcined at 1550 oC│
                        └─────────────────────┘
                                  │
                        ┌─────────────────────┐
                        │     SiC Powder      │
                        │  BET Surface Area   │
                        │    220.65 m2/g      │
                        └─────────────────────┘
         ┌────────────────────────┼────────────────────────┐
  ┌──────────────┐       ┌──────────────┐          ┌──────────────┐
  │ HF Treatment │       │ Air Treatment│          │ Air Treatment│
  │              │       │ for 3 hours  │          │ for 7 hours  │
  └──────────────┘       └──────────────┘          └──────────────┘
         │                      │                         │
  ┌──────────────┐       ┌──────────────┐          ┌──────────────┐
  │BET Surface   │       │BET Surface   │          │BET Surface   │
  │Area          │       │Area          │          │Area          │
  │221.95 m2/g   │       │333.78 m2/g   │          │362.90 m2/g   │
  └──────────────┘       └──────────────┘          └──────────────┘
         │              ┌───────┴────────┐                │
  ┌──────────────┐ ┌──────────────┐ ┌──────────────┐ ┌──────────────┐
  │Air Treatment │ │ HF Treatment │ │Steam Treatment│ │Air Treatment │
  │for 3 hours   │ │              │ │for 24 hours   │ │for 14 hours  │
  └──────────────┘ └──────────────┘ └──────────────┘ └──────────────┘
         │              │                │                │
  ┌──────────────┐ ┌──────────────┐ ┌──────────────┐ ┌──────────────┐
  │BET Surface   │ │BET Surface   │ │BET Surface   │ │BET Surface   │
  │Area          │ │Area          │ │Area          │ │Area          │
  │359.98 m2/g   │ │323.98 m2/g   │ │360.65 m2/g   │ │363.29 m2/g   │
  └──────────────┘ └──────────────┘ └──────────────┘ └──────────────┘
         │
  ┌──────────────┐
  │Steam Treatment│
  │for 24 hours   │
  └──────────────┘
         │
  ┌──────────────┐
  │BET Surface   │
  │Area          │
  │366.56 m2/g   │
  └──────────────┘
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It is clear from the results shown in Table 1 that etching with HF does not affect the internal surface area of the SiC sample significantly. This is true for the as received samples (less than a 0.6 % change) and the samples after they have been subjected to a 3 h oxidation treatment in air (less than a 3% change). This result taken together with the XRD analysis results of the same sample, which show no evidence for the presence of SiO_2, confirms that no significant amounts of residual silica are left in the samples after the carbothermal reduction reaction. The fact that the sample that is oxidized in air before the HF treatment, shows a slightly higher change in the surface area may be due to the fact that the HF is removing the passive oxide layer that may form as the result of burning the sample in air.

The BET test results indicate that the surface area of the SiC samples increases considerably after the air treatment at 420 ^{o}C for 3 h. This is likely to be due to the burning away of some of the carbon left behind after the calcination process. That little, if any, residual SiO_2 is present and that carbon is left behind

after the calcination process may be indicative that the other reactions (4, 6, and 7), in addition to (3) and (5), participate in the formation of SiC. The excess carbon that is left behind may also be an indicator of some loss of volatile Si components (e.g., SiO), which are created at the beginning of the carbothermal reduction process by solid-solid reactions at the interface between silica and carbon. Based on the proposed reaction mechanism, it is likely that the carbon matrix formed by the pyrolysis of the phenolic resin, strongly influences the final silicon carbide structure. Homogeneous mixing of the original precursors, as stated earlier, is essential in order to assure that a final SiC sample is formed, which has uniform properties including porosity and pore structure. The size and type of the silica sols one uses determines the ability of homogeneously distributing the sol with the carbon source. The finer the initial silica sol particles are, for example, the more homogeneously they distribute in the phenolic resin, and actively participate in the carbothermal reaction.

It should also be noted after a certain period of air treatment the surface area does not change significantly (note, for example, the surface areas after the 7 and 14 h treatments in air in column 3 of Table 1) indicative that most carbon inclusions are removed in the first few hours of burning in air; further heating in air does not appear to change the properties of the silicon carbide, and the sample appears to be stable.

Steam treatment is equally effective with air oxidation in removing the residual carbon. Note, furthermore, that after the carbon has been removed with air oxidation steam treatment has little effect on the surface area (compare the two values at the bottom of columns 1 and 4 in Table 1, which are more or less the same). In terms of the surface area but also of the pore size distribution (see Fig. 3) steam treatment does not affect the structure of the SiC powder after the residual carbon is removed. On the other hand, as shown in Fig. 2, the steam treatment seems to convert some of the β-SiC into α-SiC; surface area and pore size distribution (see below) appear not be sensitive indicators of this change, however. Interestingly, steam, HF, and air treatments all have little effect on the pore size distribution of the final SiC powders (see Fig. 3). Based on the above tests, the SiC powders prepared by the sol-gel process all exhibit a good hydrothermal stability, and corrosion and oxidation resistance.

3.2. The SiC Membranes

As previously noted the SiC membranes are prepared by dip-coating of substrates made of mixtures of powders which are pressed into disks and then

calcined at high temperatures. These substrates are highly porous with a bimodal pore size distribution with one sharp peak centered around 4 nm (corresponding to the finer particle size powder) together with a much broader macroporous peak centered around 150 nm corresponding to the larger size powder (see Fig. 4). The He/Ar separation factor for this substrate is close to unity and He/Ar permeance is $\sim 7.2 * 10^{(-7)}$ m^3/(m^2.Pa.sec). The effect on Ar permeance and the corresponding separation factor of coating a number SiC layers is shown in Figs. 5 and 6. The Ar permeance changes during the first coatings but remains unchanged after that. There is no dependence of the permeance on the transmembrane pressure gradient, which is also a good indicator of the lack of any substantial convective flow contributions to the membrane transport. These observations are also validated by the behavior of the separation factor with the number of coatings (Fig 6). After the third coating the measured separation factors are very close to the ideal Knudsen value of 3.16. AFM has also been used to study the surface morphology of the sol-gel coated samples. Figure 7 shows the AFM image of the SiC sol-gel membrane. There are no cracks and/or pinholes observed in the membrane layer, and the surface appears to be relatively smooth. Figure 8 shows the XRD pattern of the SiC membrane together with the XRD pattern of one of the powders prepared under similar conditions. The two XRD patterns are indistinguishable with the peaks corresponding primarily to β-SiC and with a very small quantity of α-SiC phase also being present.

The SiC membranes were also subjected to the same hydrothermal test the various powders went through. The test, as previously, was carried out by exposing the membranes at 350 ^{o}C to a flowing mixture consisting of 50-mol% of water and 50-mol% of argon for a period of 30 h (the test was terminated after this period because there was no noticeable change in the membrane properties). During the test the argon permeation rate of through the membrane was constantly monitored, and the results are shown in Fig. 9. The argon permeance remained constant throughout the whole period the membrane was exposed to steam. After the hydrothermal test the membrane separation characteristics were also studied by measuring the permeation rate of He and Ar. No noticeable changes were observed in the membrane transport characteristics, as can be seen in Figs. 5 and 6 which show the Ar permeance and the He/Ar separation factor as a function of transmembrane pressure gradient for the membrane before and after the hydrothermal test. Figure 10 shows an SEM picture of a cross section of the SiC membrane after the hydrothermal stability test. The sol-gel SiC thin film (~4-5 μm thick) lies on the top of the macroporous SiC disk. It appears to be strongly adhering without any is visible cracks or pinholes developing after the hydrothermal stability test.

To further investigate the ability of these materials to withstand the various corrosive environments, the various samples were analyzed by XPS. The XPS data are collected by a Perkin-Elmer /Physical Electronics Division model 5100 X-ray photoelectron spectrometer with a non-monochromatic Al K_α 1486.6 eV radiation source (15 kV, 300 W). Data acquisition and instrument control is performed using an RBD model 147 controller with Augerscan™ software. The samples, after being subjected to the various treatments, they are placed into the analysis chamber and allowed to outgas until a vacuum of $< 1 \times 10^{-7}$ torr had been restored (typical analysis pressure was in the range of $1 - 8 \times 10^{-8}$ torr). Figure 11, for example, shows the XPS results of a powder SiC sample, which after being treated by HF for 5 h, air at 420^oC for 3 h was subjected to a steam treatment. There is a strong peak at 100.4-101.0eV corresponding to SiC, which is indicative that the sample is silicon carbide (deconvolution of the spectra indicates the SiC content to be in excess of 94%). A small side shoulder at 103.0-103.3eV corresponds to a trace impurity of SiO_2, which may be either a remnant of the original sol, or most likely due to the surface oxidation of the SiC as a result of the air oxidation and steam treatments. The XPS results seem to be consistent with the results of the XRD analysis.

4. CONCLUSIONS

Silicon carbide asymmetric membranes and powders have been prepared by a sol-gel processing step followed by a carbothermal reduction reaction between the silica and carbon precursors. The resulting materials consist mostly of SiC and some residual carbon. This carbon is easily removed by an air or steam treatment without any negative impact on the mechanical properties of the membrane. Permeation studies of the SiC membranes show ideal separation factors for single gases, which are close to the Knudsen values. This means that the resulting films have no substantial fraction of macroporous cracks and pinholes. They are, therefore, promising substrates for the preparation of permselective microporous membranes by either CVD or polymeric precursor pyrolysis techniques or for ultrafiltration or nanofiltration applications involving corrosive liquids. The membranes are resistant to treatment by HF, oxidation by air, and prolonged exposure to steam at high temperatures.

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LIST OF ACRONYMS AND ABBREVIATIONS

AFM:	Atomic Force Microscopy
CVD:	Chemical Vapor Deposition
HF:	Hydrofluoric Acid
PAN:	Polyacrylonitrile
PSD:	Pore size distribution
PTMS:	Phenyltrimethoxysilane
SEM:	Scanning Electron Microscopy
TEOS:	Tetraethylorthosilicate
TPS:	Tripropyl Silane
WGS:	Water-Gas-Shift
XPS:	X-Ray Photospectroscopy
XRD:	X-Ray Diffraction
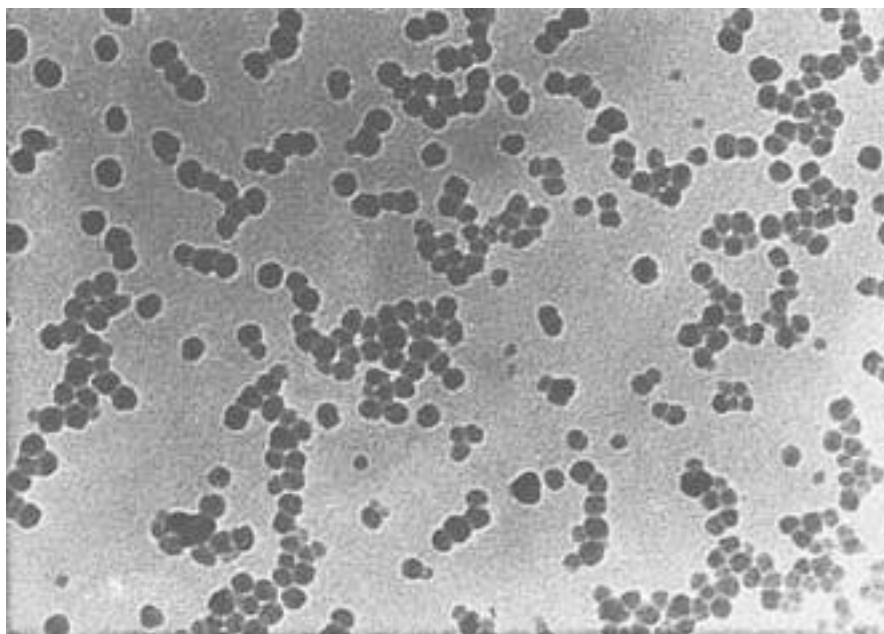
Figure 1   The TEM picture of the organo-silica sol type IPAST with particle size 8-11 nm,   provided by Nissan Chemical Industries, Ltd.
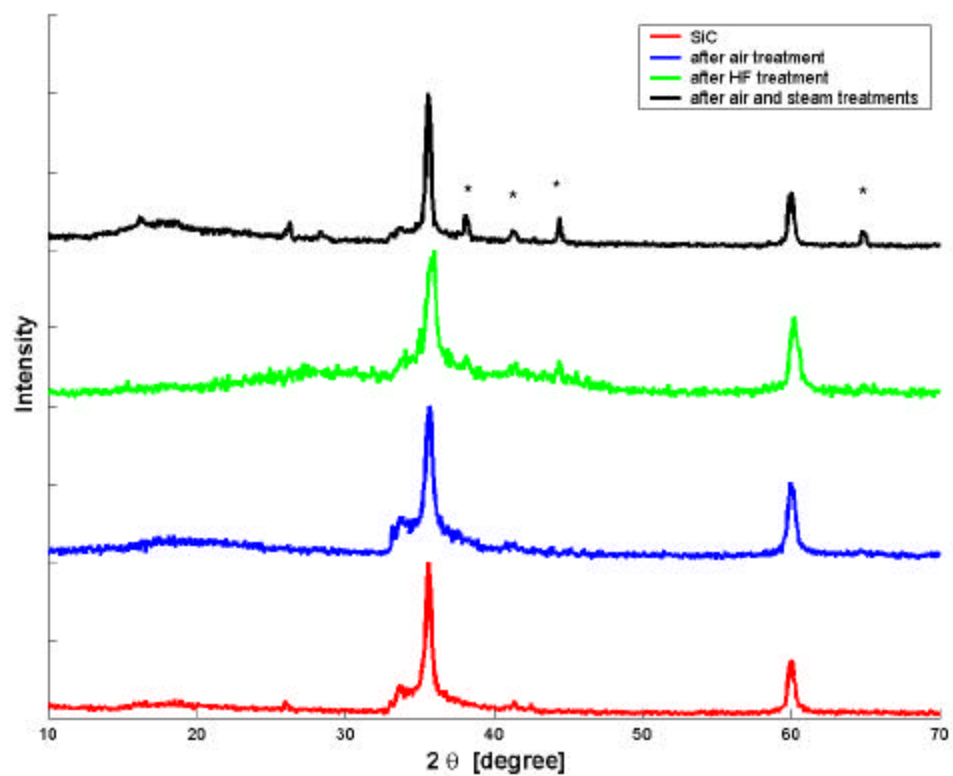
Figure 2. The XRD pattern of a SiC powder treated with HF, air, and steam. * signifies the peaks corresponding to the (6H) phase.
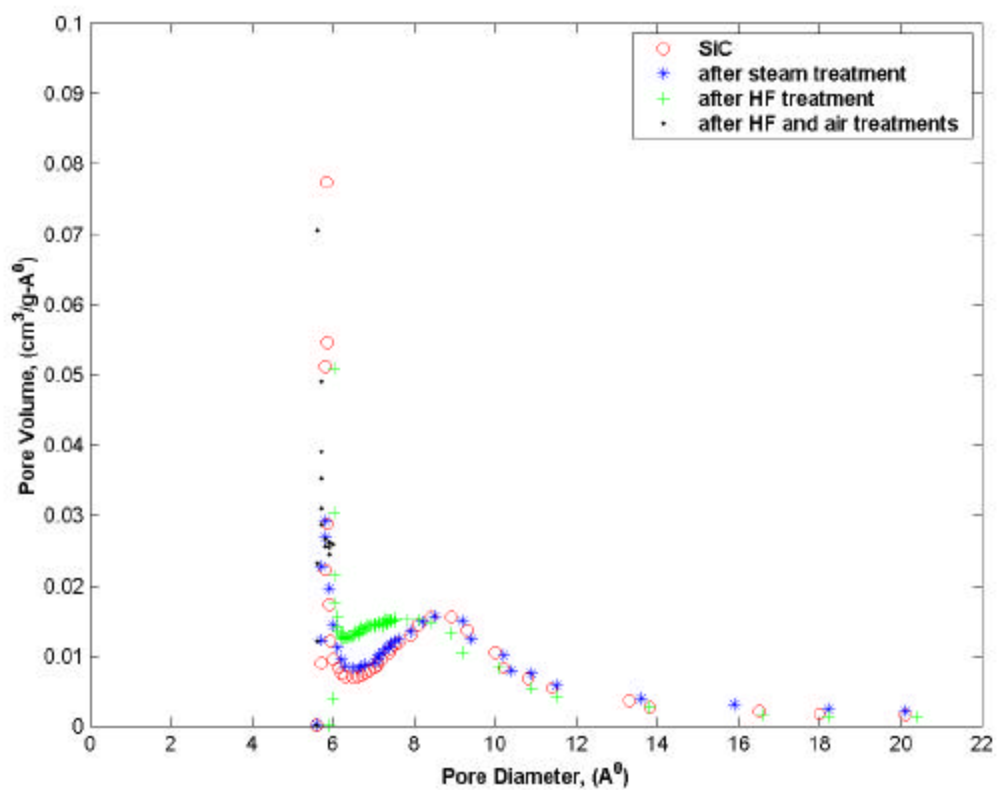
Figure 3.   The pore size distribution of the SiC powders after various treatments
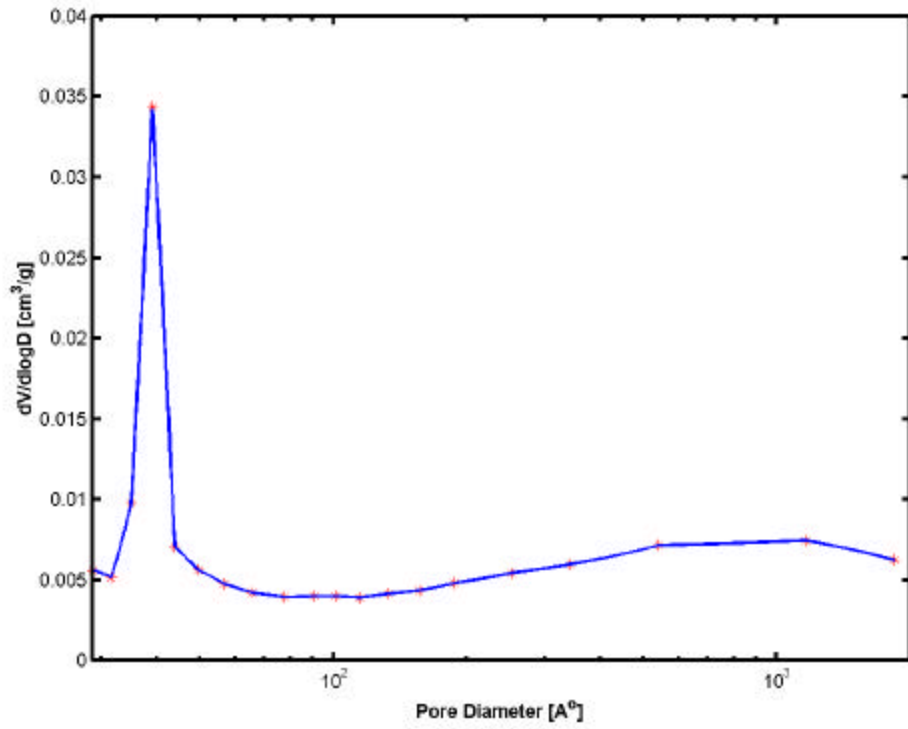
Figure 4   The dV/dlogD of the SiC substrate utilized in the preparation of the Sol-Gel membranes.
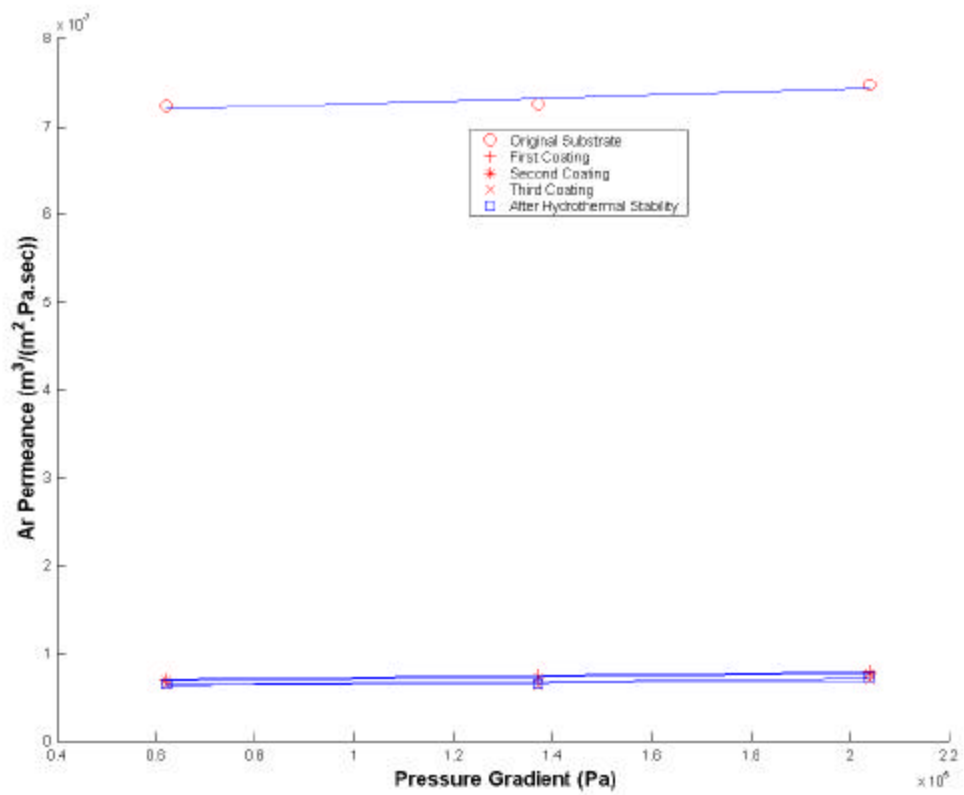
Figure 5.   The argon permeance of the membrane as a function of the
pressure gradient and the number of coatings.
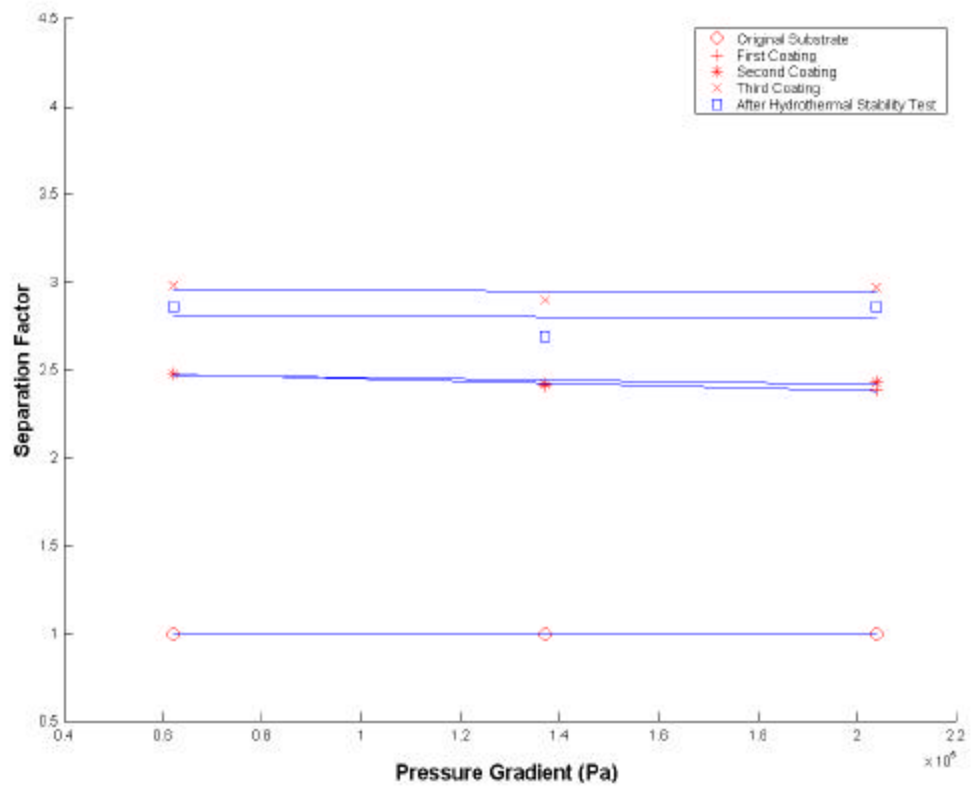
Figure 6.   The separation factor of the membrane as a function of the pressure gradient and the number of coatings.
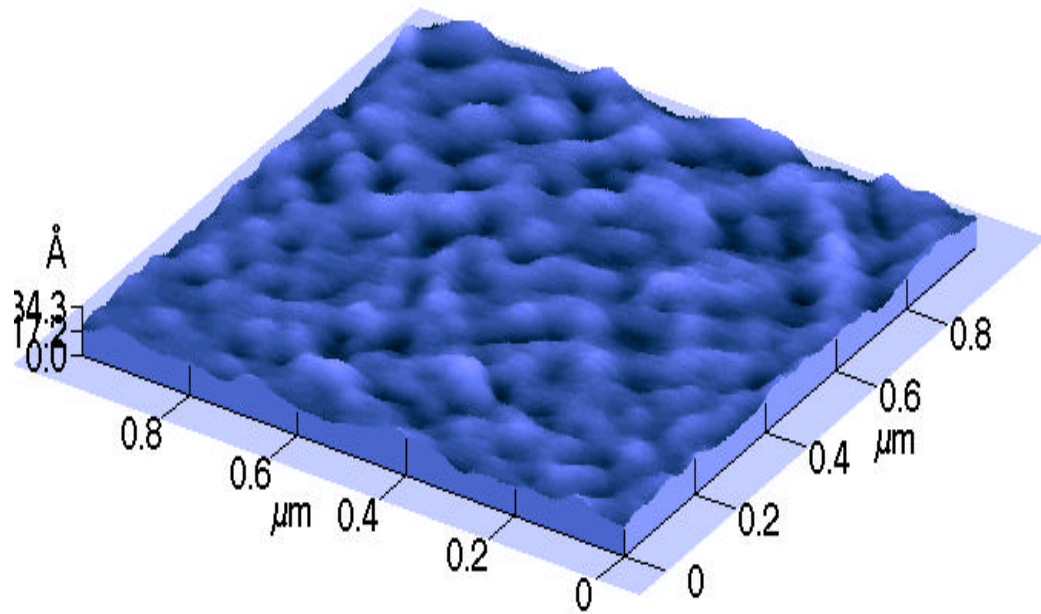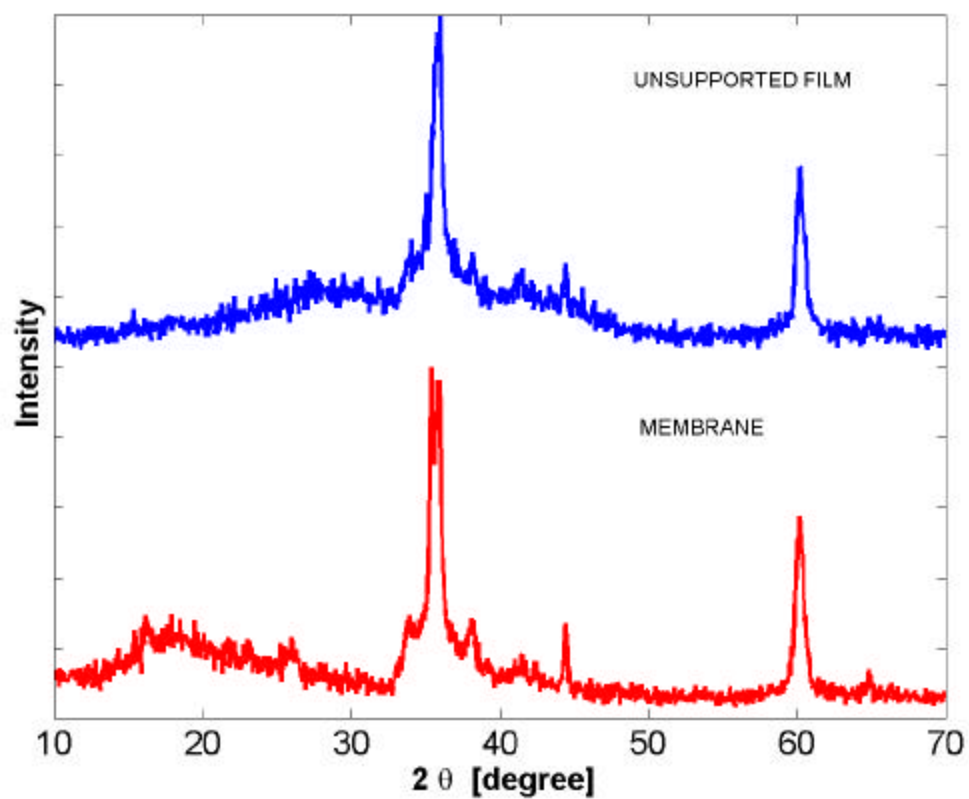
Figure 7. AFM image of the SiC sol-gel membrane

Figure 8   The XRD patterns of the SiC membrane and the unsupported film
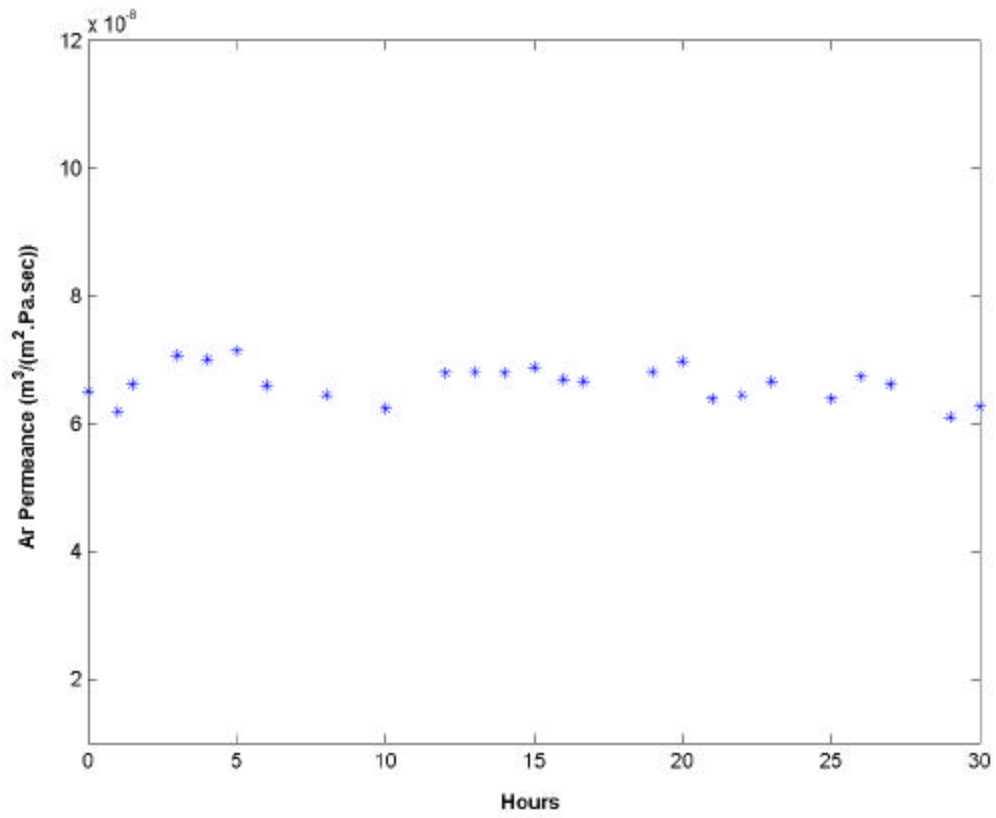   (powder) prepared by the same techniques.

Figure 9. The membrane argon permeance during exposure to steam.
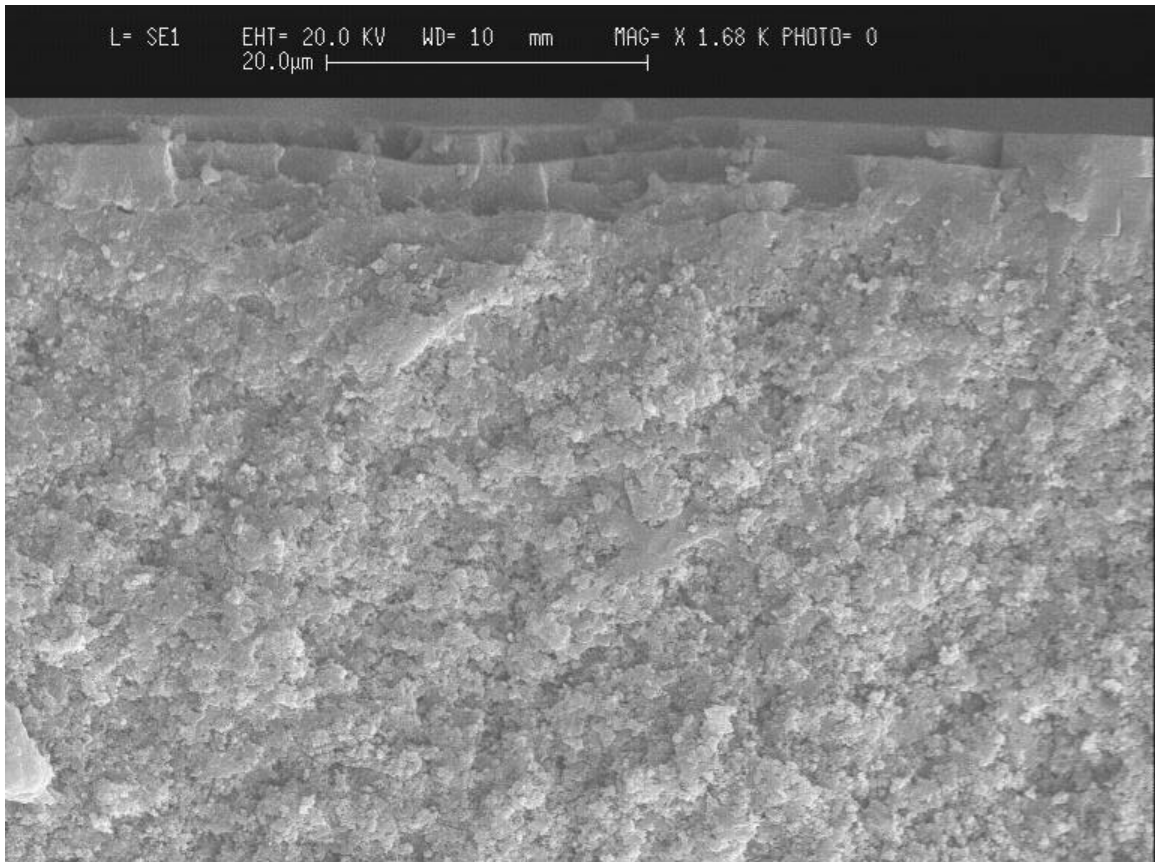
Figure 10.   A SEM picture of the cross section of the SiC membrane prepared
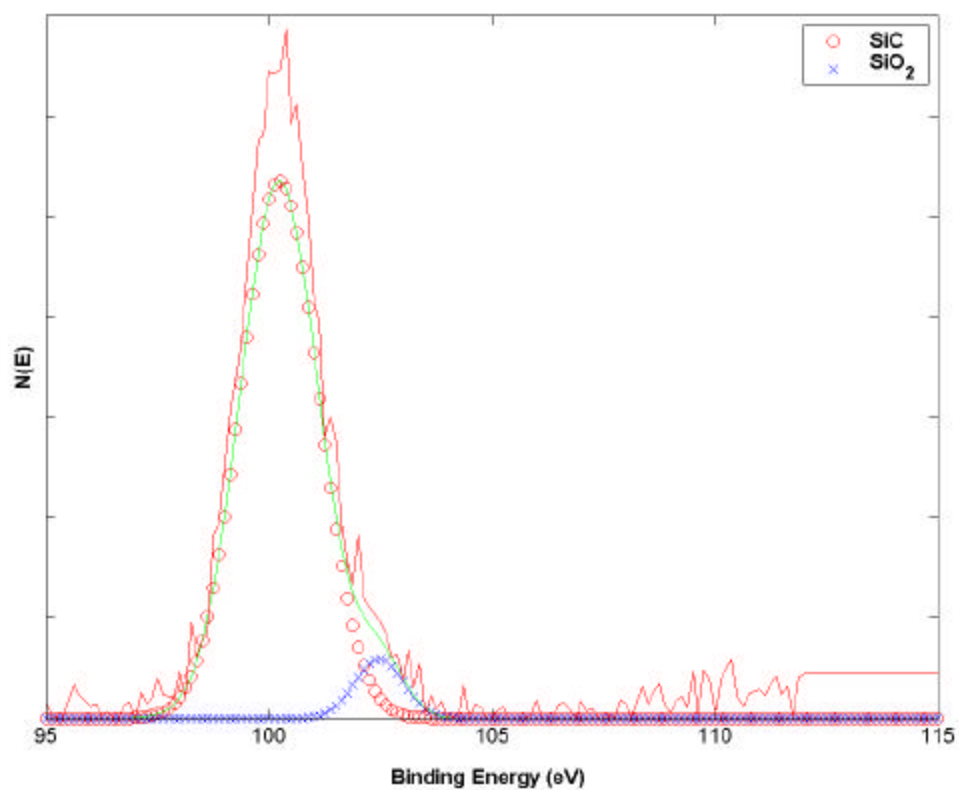   by Sol-Gel technique

Figure 11.   The XPS spectrum of the SiC powder sample. The superimposed peaks correspond to SiC at 100.4-101.0 ev and SiO_2 at 103.0-103.3 ev, respectively.