

Proton-Conducting Dense Ceramic Membranes for Hydrogen Separation

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ABSTRACT

This project is aimed at preparation of thin (1-10² m) membranes of a modified strontium ceramic material with improved hydrogen permeance on mesoporous substrates. The research work conducted in this reporting period was focused on the following three aspects: (1) preparation of thick proton-conducting ceramic membranes and synthesis of porous substrates as support for thin proton-conducting ceramic film, (2) setting up RF sputter deposition unit for deposition of thin ceramic films and performing deposition experiments with the sputter deposition unit, and (3) modeling hydrogen permeation through the proton-conducting ceramic membranes. Proton-conducting thulium doped strontium cerate membranes were reproducibly prepared by the citrate method. Mesoporous ceria membranes were fabricated by a sol-gel method. The membranes will be used as the substrate for coating thin strontium cerate films. A magnetron sputter deposition unit was set up and good quality thin metal alloy films were formed on the mesoporous substrates by an alternative deposition method with the sputter deposition unit. A theoretical model has been developed for hydrogen permeation through proton conducting ceramic membranes. This model can be used to quantitatively describe the hydrogen permeation data.

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INTRODUCTION

Proton-conducting dense ceramic membranes have become a promising group of inorganic membranes with high selectivity for hydrogen permeation^[1-6] since Iwahara and coworkers discovered proton-conduction in SrCeO₃ based perovskite type ceramics in high temperatures in the 1980's^[7]. The major problem with the SrCeO₃ based ceramic membranes is their low electronic conductivity, which leads to low hydrogen permeability. Therefore, the effective way to improve the electronic conductivity of this kind of membranes is to dope metals with lower ionization potential. Recently, thulium doped SrCeO₃ perovskite materials were prepared in our lab^[1]. A relatively high hydrogen permeation flux for 2 mm thick thulium doped SrCeO₃ (SCTm) was obtained (about 0.5×10^{-7} mol/cm².s at 900^oC). Further study has shown that the hydrogen permeation is inversely proportional to the thickness of the membrane. Obviously, reduction of the membrane thickness would be effective in further improving the hydrogen permeation flux for the SCTm ceramic membrane. The objective of this project is to synthesize thin SCTm membranes and investigate hydrogen permeation properties of these membranes.

EXECUTIVE SUMMARY

Citrate method was used to prepare $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_3$ (SCTm) powder. Symmetric mixed-conducting SCTm membranes were produced by the press and sintering method. A series of characterization experiments were performed on the obtained membranes, such as XRD, gas tightness checking with helium permeation, and electrical conductivity measurement. These results show that these SCTm membranes have the desired perovskite structure, gas-tightness, and electrical conductivity. Stable cerium oxide sol was prepared by the sol-gel method. Thin films of cerium oxide were coated on the macroporous alumina support. The cerium oxide layers have a pore size in the range of 5-10 nm. Mesoporous ceria membranes will be used as the support for the strontium cerate based proton-conducting ceramic thin films.

A magnetron RF sputtering system was set up in our lab. RF, not DC, sputtering, is required for coating the thin ceramic films. A series of testing experiments were conducted with this system. The targets included palladium, alloy of palladium and silver, tantalum, copper, and the porous γ -alumina and α -alumina coated α -alumina were used as the substrates. This system is now fully functioning, allowing control of substrate temperature, substrate to target distance, and sputtering power. Alternative deposition was successfully performed with pure palladium and pure copper as the targets. Two permeation systems were modified or set up for membrane characterization. These permeation systems have been used to characterize the dense proton-conducting ceramic membranes, thin metallic membranes, and mesoporous membranes described above.

A mathematical model was developed for hydrogen permeation through proton conducting ceramic membranes based on the ambipolar diffusion theory. A general equation was derived that correlates hydrogen permeation flux to concentrations and diffusion coefficients of the three charged species (proton, electron and electron-hole). The equation can be simplified to analytic expressions relating the hydrogen permeation flux to the hydrogen partial pressures at upstream and downstream sides for special cases. The model was compared to experimental data obtained in our lab and good agreement is obtained by the model and experimental data. Two papers on the modeling were respectively presented in a conference and submitted to a refereed journal.

EXPERIMENTAL

Preparation and Characterization of SCTm Dense Membranes

The SCTm perovskite-type materials were prepared by the citrate method from the following metal nitrate precursors: $\text{Sr}(\text{NO}_3)_2$ (purity 99%, Aldrich), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purity 99.5%, Alfa), $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Alpha, 99.9%), and citric acid (purity 99.5%, Alfa). In experiments, 14.814 g $\text{Sr}(\text{NO}_3)_2$, 28.869 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 1.557 g $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 600 ml distilled water. 40.35 g citric acid was added to the solution for adjusting the pH to 3.5. Then this solution was heated to 96°C – 100°C , where polymerization reaction took place for 5 hrs with stirring in a refluxed-mode. Subsequently, the water was evaporated at 100°C and a condensation reaction happened. Finally, gel-like material was formed. After dried at 110°C for 24 hours, the gel-like material became a sponge-like and brittle material, which was followed by self-ignition at 400°C for 30 min.

The material after self-ignition was ground to powder and calcinated at 600 – 800°C for 10 hrs to remove the residual organic compounds. The powder was ground again by agate mortar and pressed into disks under a hydraulic pressure of 130MPa. The green disks were sintered at 1500°C for 24 hrs in a furnace with a ramp rate of $2^\circ\text{C}/\text{min}$ during heating and cooling cycles. Finally, dense, thick SCTm membrane disks were obtained.

X-ray diffraction (XRD) analysis of the powders or disks was carried out by Siemens Kristalloflex D500 diffractometer, with Cu K α radiation and 2θ changed from 20 to 70° . Gas-tightness of SCTm disks was checked by the unsteady state permeation cell system, as shown in Fig.1. No flux was observed, confirming the gas-tightness of the obtained disks. Electric conductivity was also carried out by the four-point method to further verify the composition and phase structure of the obtained samples.

A hydrogen permeation system was set up, as shown in Fig.2. The membrane was sealed by a ceramic sealant (40% SCTm powder, 50 Pyrex glass powder and 10% NaAlO_2). During permeation measurement, the system was heated to 950°C and kept for 0.5 hr to ensure melting of the seal. Then the system was cooled down to check the leakage by gas chromatography. H_2/He and O_2/N_2 were introduced to the both sides of the membrane respectively. The hydrogen flux was calculated from the rate of water produced in the oxygen side. The partial pressure of water vapor was measured by a Thermohygrometer humidity sensor (Cole-Parmer).

Synthesis of Porous Substrate as Support for Thin Film

For membrane applications, the thin SCTm films should be supported on a porous substrate. Mesoporous CeO_2 was chosen as the top layer of substrate and macroporous γ -alumina as the substrate support. The mesopores of the CeO_2 would facilitate formation of a gas-tight thin SCTm film. CeO_2 is also chemically more compatible with SCTm material. A sol-gel method was used for preparation of the CeO_2 substrates. Since the technique used to prepare the substrate layer is similar to that for preparation of mesoporous γ -alumina membranes, synthesis of γ -alumina membranes on macroporous γ -alumina supports was also studied in the past year.

?-Alumina Supports and ?-Alumina Coated Substrate

The porous ?-alumina disks (2 mm thick with 0.2 μm average pore diameter) were prepared by pressing ?-alumina powder (Alcoa) with a mechanical press (Dake Corporation) at a pressure of 10MPa, followed by sintering at 1150⁰C for 30 hrs in a temperature programmable furnace. One side of each disk was polished with sandpapers #320, #500 and #800 successively and examined visually as well as by a light microscope for the defects before coating. Gas permeation was measured by the unsteady state system.

Boehmite sol was prepared by sol gel method. 1 mol of alumina-tri-sec-butoxide (MW=246.33g/mol, 97% purity, Alfa) was gradually added to 1 liter water heated at 70-90⁰C while stirring for half to one hour. Then 70 ml 1M HNO₃ was added to adjust the pH. The final 1M boehmite sol was obtained after refluxing at 90-100⁰C for 10 hrs. The pore structure of the unsupported ?-alumina film after drying and calcination was characterized by nitrogen adsorption porosimetry (ASAP 2000, Micromeritics). PVA solution (30g/l, MW=72,000g/mole, Alfa) doped boehmite sol was prepared (20 ml boehmite sol vs 13 ml PVA solution) for dip-coating. The dip-coated disk underwent a temperature programmed calcination process. In order to improve the quality of ?-alumina layer, multiple coating was applied. Gas permeation was measured with the ?-alumina before and after coated ?-alumina by the steady state system.

Cerium Oxide Coated Substrates

Stable hydrous cerium oxide sol was prepared from cerium nitrate salt. Cerium nitrate hexahydrated solution (0.1M), Ce(NO₃)₃·6H₂O was mixed with hydrogen peroxide, H₂O₂ (29.5wt%), at 5⁰C while stirring with the volume ratio of 3:1. After 10 minutes, ammonium hydroxide solution was added to increase the pH till 10. By precipitation, solution and precipitate were separated. The precipitate was dried at 80⁰C overnight followed by calcination in air at 450⁰C for 3 hrs. The solution was hydrothermally treated at 180⁰C for 4 hrs under autogenous pressure without stirring to obtain cerium oxide. After cooling down, the yellowish precipitate was treated in the same way as above.

With the obtained CeO₂ powder, several stable hydrous cerium oxide sols were prepared. The precipitate before drying was dispersed in DI water, then peptized with addition of 1M HNO₃ solution, while stirring and heating at 70⁰C, until a clear sol was obtained. The supported cerium oxide membranes were prepared by dip-coating the cerium oxide sol on the porous alpha alumina disks. Unsupported cerium oxide membranes were prepared by drying a given amount cerium oxide sol in petri-dishes. The pore structure and gas permeation properties of the membranes were characterized by nitrogen adsorption and gas permeation.

RF Sputtering Deposition and Characterization

In this project, RF sputtering and inorganic-organic polymeric sol coating have been chosen as the two methods for deposition of thin films of SCTm on the porous ceramic supports. The final SCTm membrane will consist of a thick (2 mm),

macroporous γ -alumina support, thin (5 μ m) mesoporous CeO_2 intermediate layer, and thin (1-10 μ m), dense SCTm film.

A magnetron RF sputtering system was set up in our laboratory, as shown in Fig.3. Some problems of contact and heater were solved. A series of test deposition experiments were conducted with various targets under different conditions, followed by characterization experiments of gas tightness and XRD. The targets included palladium silver alloy, tantalum, pure palladium and copper. Deposition experiments were conducted under different conditions (different substrates γ -alumina and γ -alumina coated γ -alumina), substrate temperatures during deposition (from room temperature to 300 $^{\circ}$ C), deposition powers (from 40 to 200 W), and deposition time (from 10 minutes to 75 minutes).

Alternative deposition with pure palladium and pure copper as the target was performed at the substrate temperature of 300 $^{\circ}$ C with the power of 75W. The order for this alternative deposition is listed as follows (target and sputter deposition time): Pd-15 min, Cu-8 min, Pd-12min, Cu-8min, Pd-12min, Cu-8min. The total deposition time was 63 min.(Pd-62%, Cu-38%). The substrate used was γ -alumina. The gas tightness and phase structure of the deposited film were examined. These experiments were done to simulate alternative deposition of Ce, Sr, and Tm for preparation of thin SCTm films on porous substrates.

Setup of Gas Permeation Measurement

Two gas permeation measurement systems were set up. One is used to check gas tightness by the unsteady state method with helium (see Fig 1). The system was evacuated by vacuum pump and flushed with helium for enough time. Then helium was introduced to the upstream of the membrane. From the data of pressure change with respect to time, the gas permeance through the membrane was calculated. The other system is designed to measure the hydrogen permeance at high temperature (600-900 $^{\circ}$ C). The membrane is seated in the middle of the tube furnace. Hydrogen and helium are introduced from the upstream of the membrane while nitrogen and oxygen from the downstream. GC is used to check the sealing effect of the membrane by measuring the nitrogen content at the upstream flow. A humidity sensor is used to measure the vapor production at the downstream due to the hydrogen permeation and combination with oxygen.

RESULTS AND DISCUSSION

Synthesis of SCTm membrane and Porous Membrane Substrates

Fig. 4 shows XRD result of the obtained SCTm sample. For comparison, the XRD pattern of a well studied $\text{SrCe}_{0.95}\text{Tb}_{0.05}\text{O}_3$ (SCTb) is also given in the figure. These XRD patterns indicate that the SCTm sample has the desired perovskite structure. SCTm membranes of 20 mm in diameter and 1-2 mm in thickness were prepared. These membranes were also gas tight as confirmed by the helium permeation tests.

Good quality porous γ -alumina disks of 20 mm in diameter and 2 mm in thickness were obtained. The unsupported γ -alumina membrane has a surface area of 433 m^2/g and pore diameter of 3.7 nm. Supported γ -alumina membranes (on α -alumina) were prepared by the dip-coating method. Helium permeation of γ -alumina before and after coated γ -alumina is plotted in Fig.5. Good permeation reduction has been achieved after γ -alumina was coated with γ -alumina.

Stable CeO_2 sols were prepared by the sol-gel method. The unsupported CeO_2 membranes after calcinations at 450°C have a surface area of about 141 m^2/g and pore diameter of 5 nm. The XRD analysis shows that the CeO_2 membranes have a fluorite-type crystalline structure, as shown in Fig. 6. Supported CeO_2 membranes were prepared by dip-coating the CeO_2 sol on the γ -alumina supports. Multiple-coating was required due to lower concentration of the CeO_2 sols. We are continuing experiments on characterizing gas permeation properties of the new mesoporous CeO_2 membranes.

Sputtering Deposition of Metal Membranes

A series of experiments on deposition of Pd, Pd-Ag and Pd-Cu films were performed with the magnetron RF sputter unit. Both γ -alumina and α -alumina coated α -alumina disks were used as the substrates. The results obtained are summarized below.

The deposition rate with the RF mode is lower than that with the DC mode. This is due to the different deposition mechanism. In the DC mode at the power of 75 W, the deposition rate for Pd/Ag alloy is about 4 $\mu\text{m}/\text{hr}$. while in the RF mode, it is 1 $\mu\text{m}/\text{hr}$. Tantalum has a lower deposition rate (0.75 $\mu\text{m}/\text{hr}$ in the RF mode) than Pd/Ag alloy. The deposition rate can be considered as one of the intrinsic attribute for a certain sputtering system. It is determined by quite a few factors, such as the geometry, total space and wall surface of the chamber, and the size and position of the magnetron. Targets of different materials have different deposition rate in the same sputtering system due to differences in the bonding force between the atoms and atomic weight which would affect rate of the atom precipitation during deposition.

The top layer surface quality of the substrate is most critical to gas-tightness of the thin film desposited. For example, in the RF mode at the power of 75 W, 10 minutes deposition of Pd/Ag could result in 10-fold reduction in helium flux ($0.76 \times 10^{-6} \text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$) for good γ -alumina coated α -alumina substrate while 30 minute deposition is needed to get the same gas-tightness for α -alumina substrate which has much larger pores than the γ -alumina substrate.

Substrate temperature during deposition plays an important role in obtaining gas tight thin film. Higher temperature favors formation of gas tight thin film and also facilitates annealing of different metal layers deposited when alternative deposition is used. The upper-limit of substrate temperature is determined by the equipment. The optimized conditions for our system are: the deposition power is 75 W and substrate temperature is 300°C.

Good quality Pd/Cu membranes were obtained by alternative depositions using Pd and Cu targets. The XRD analysis (Fig.7) shows that the alloy of Pd/Cu was partially formed during the deposition compared with the XRD result of Pd/Cu after annealing at the temperature of 500°C with helium flow. This is because the film is rather thin (<1 micron) and the substrate temperature was 300°C during deposition. These two factors facilitate partial annealing during the sputter deposition. Pd/Cu film on the γ -alumina substrate obtained with 63 minute alternative deposition of Pd and Cu targets is very gas-tight, with a helium permeance of $0.56 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$, much lower than that for the support ($1.7 \times 10^{-5} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$). The success of the alternative deposition is important to sputter deposition of SCTm perovskite film as similar approach will be used to obtain the metal films of Sr, Ce and Tm alloy, followed by oxidation reaction to form SCTm oxide film.

Hydrogen Permeation Modeling

Hydrogen permeation through dense proton-conducting ceramic membranes was modeled based on the ambipolar diffusion theory by considering three moving charged species: proton, electron and electronic hole. The modeling results in a general flux equation from which explicit equations for hydrogen permeation flux can be derived for proton-conducting ceramic membranes operated in hydrogen separation and membrane reactor modes. The final expressions relate hydrogen permeation flux to the experimentally measurable variables including membrane thickness, upstream and downstream hydrogen partial pressures, and temperature. The parameters in these hydrogen permeation flux expressions include electron, hole or proton conductivity or concentration at a reference state ($P_{\text{H}_2}=1 \text{ atm}$) with explicit physical meaning, which can be regressed from the experimental hydrogen permeation data or obtained by independently designed measurement.

For hydrogen permeation through proton-conducting ceramic membranes with proton transference number closed to one, the model gives the following hydrogen permeation flux equation:

$$J_{\text{H}_2} = \frac{RT}{2LF^2} (\sigma_e^o P_{\text{H}_2}^{1/2} - \sigma_h^o P_{\text{H}_2}''^{1/2}) \quad (1)$$

where σ_h^o and σ_e^o are the electronic-hole and electron conductivity at $P_{\text{H}_2}=1 \text{ atm}$, P_{H_2} and P_{H_2}'' are the hydrogen partial pressure in the upstream and downstream of the membranes. It should be noted that in this case the hydrogen partial pressure P_{H_2}'' can not be measured directly because air is present at the downstream side. P_{H_2} in Eq. (1) should be calculated from the experimentally measurable oxygen and water vapor partial

pressures in the downstream side using a thermodynamic equilibrium relationship. Eq. (1) shows that the hydrogen permeation flux increases with increasing upstream pressure and decreasing downstream pressure. σ_h^o is usually very small. However, the equilibrium $P_{H_2}^o$ in air-water mixture is also very small. As a result, the second term in Eq. (1) can be very significant.

Eq.(1) was compared to hydrogen permeation data for 1.2 mm SCTm membrane with upstream hydrogen partial pressure varied from 0.02 to 0.20 atm at fixed downstream oxygen pressure (0.2 atm), and for a 1.6 mm SCTm membrane with downstream oxygen partial pressure varied from 0.1 to 1 atm at fixed upstream hydrogen partial pressure (0.1 atm). The regressed values of the two constants, σ_e^o and σ_h^o , electron and hole conductivity at $P_{H_2}=1$ atm, are 7.40×10^{-3} S/cm and 3.22×10^{-8} S/cm respectively. With these values for two parameters σ_e^o and σ_h^o , the hydrogen flux under different upstream and downstream hydrogen partial pressures were calculated from Eq. (1) and compared with the experimental data as shown in Figs. 8 and 9. The model equation agrees with the experimental data.

The electronic conductivity data obtained have the reasonable values for proton-conducting ceramics. We reported the total conductivity of SCTm in 10% hydrogen ($P_{H_2}=0.1$ atm) of about 1×10^{-2} S/cm at 900°C ^[3]. Based on the values of σ_e^o and σ_h^o measured, the electron and electron-hole conductivities at $P_{H_2}=0.1$ atm are respectively about 2.3×10^{-3} S/cm and 1.0×10^{-7} S/cm. Since the proton-conductivity is larger than the electron-conductivity for SCTm, it is acceptable to use Eq. (1) to approximate the hydrogen permeation flux for the present case.

PUBLICATIONS FROM THIS PROJECT

The following papers have been prepared summarizing the results obtained from this project:

X.Qi, S. Cheng, Y.S. Lin, "Modeling and experimental study of hydrogen permeation through proton conducting ceramic membranes", Proceedings of 4th Internal. Symp. on Ionic and Mixed-Conducting Ceramics", 2001 ESC and ISE Joint International Meeting (Paper 1525), San Francisco, Sept. 2-7, 2001 (Accepted)

Xiwang Qi and Y.S. Lin, "Modeling of Hydrogen Permeation through Proton Conducting Ceramic Membranes", *Solid State Ionics*, Submitted (2001)

CONCLUSIONS

In the first year of the three-year project, we have set up or modified all the equipment and apparatus for the experiments required for the project. These include magnetron RF sputter deposition unit and gas permeation system. Mesoporous substrates were successfully prepared by the sol-gel methods. Dense, thick Tm doped Sr-Ce perovskite membranes of desired crystalline structure were prepared and their hydrogen permeation fluxes were experimentally determined. Theoretical model for hydrogen permeation through the proton-conducting ceramic was established and compared with the experimental data. The model allows analysis of the experimental data and prediction of the hydrogen permeation properties of the proton-conducting ceramic membranes. Various deposition experiments (including alternative deposition with different metal targets) were performed with the magnetron RF sputter system. Good quality of metal films on porous substrates were obtained. The successful preparation of mesoporous cerium oxide substrate and alternative deposition of Pd/Cu guarantee a higher success rate of fabricating thin SCTm proton-conducting ceramic films on porous substrate by the sputter deposition method.

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- 2) Xiwang Qi and Y.S. Lin, Electrical Conducting Properties of Proton-conducting Terbium Doped Strontium Cerate Membranes, *Solid State Ionics*, 120 (1-4) (1999) 85.
- 3) Xiwang Qi and Y.S. Lin, Electrical Conduction and Hydrogen Permeation through Mixed Proton-Conducting Strontium Cerate Membranes, *Solid State Ionics*, 130 (1-2) (2000) 149.
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- 7) H. Iwahara, T. Esaka, H. Uchida, T. Yamauchi and K. Ogaki, High temperature type protonic conductor based on SrCeO_3 and its application to the extraction of hydrogen gas, *Solid State Ionics*, 18-19 (1986) 1003

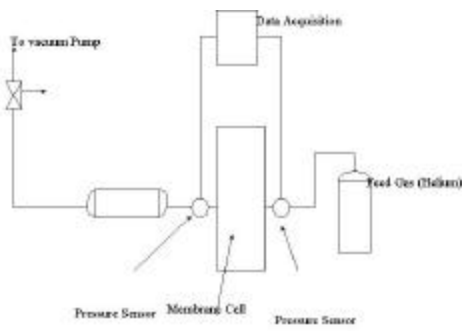


Figure 1 Setup of Unsteady-state Gas Permeation System

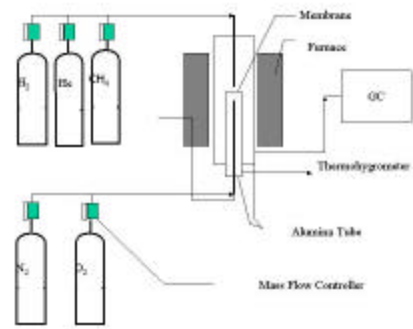


Figure 2 Setup for Hydrogen Permeation Measurements at High Temperature

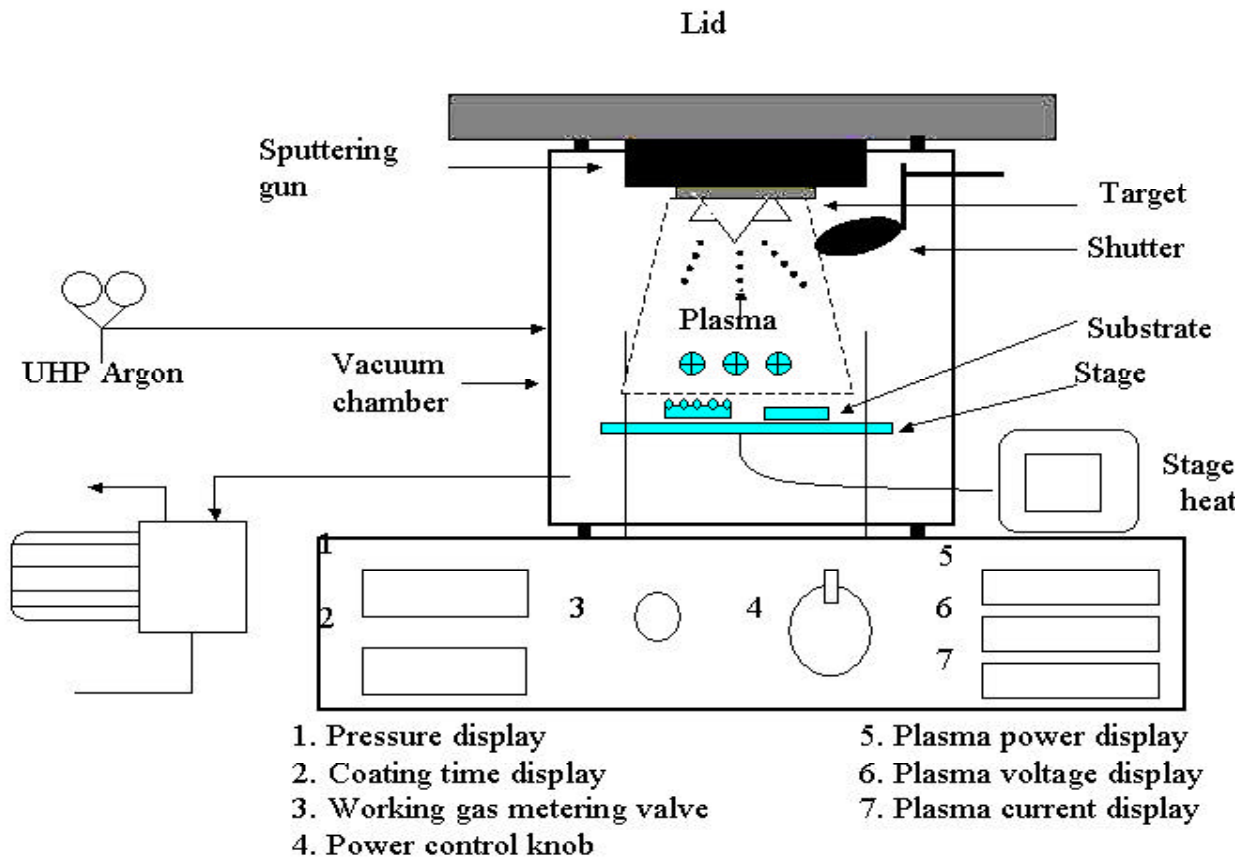


Figure 3 Magnetron Sputtering System

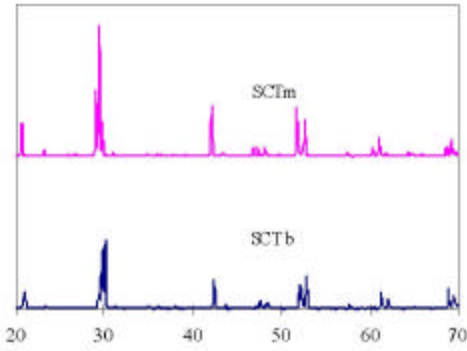


Figure 4 XRD Patterns of SCTm and SCTb

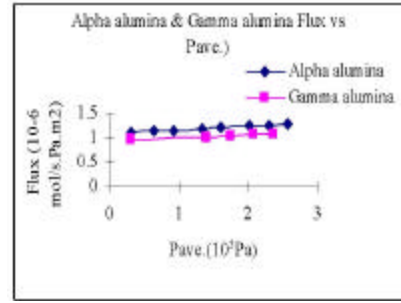


Figure 5 Helium Permeation on γ -Alumina Support before and after Coated with γ -Alumina

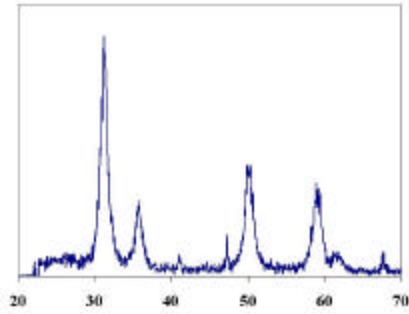


Figure 6 XRD Pattern of Sol-gel Derived CeO₂

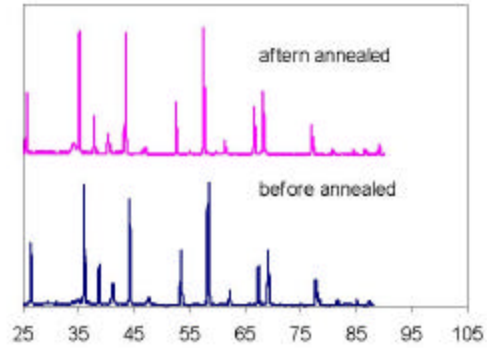


Figure 7 XRD Patterns of Pd/Cu Thin Film on γ -Alumina Substrate before and after Annealing

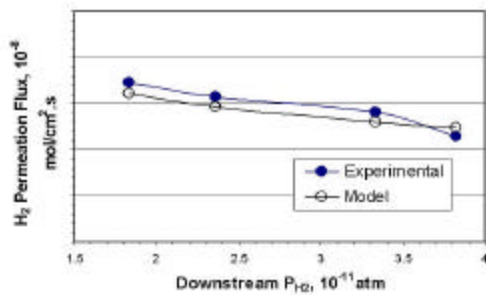


Figure 8 Comparison of Hydrogen Flux for 1.6 mm SCTm Membrane

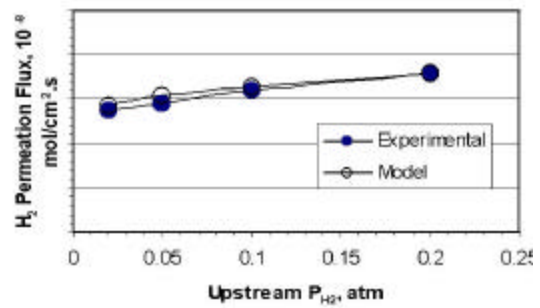


Figure 9 Comparison of Hydrogen Flux for 1.2 mm SCTm Membrane