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**A Novel Membrane Reactor for Direct Hydrogen Production from Coal**

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## DISCLAIMER

**ABSTRACT**

Gas Technology Institute is developing a novel concept of membrane gasifier for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal-derived synthesis gases. The objective of this project is to determine the technical and economic feasibility of this concept by screening, testing and identifying potential candidate membranes under high temperature, high pressure, and harsh environments of the coal gasification conditions. The best performing membranes will be selected for preliminary reactor design and cost estimates.

To evaluate the performances of the candidate membranes under the gasification conditions, a high temperature/high pressure hydrogen permeation unit has been constructed in this project. The unit is designed to operate at temperatures up to 1100$^{o}$C and pressures to 60 atm for evaluation of ceramic membranes such as mixed ionic conducting membrane. Several perovskite membranes based on the formulations of BCN ($BaCe_{0.8}Nd_{0.2}O_{3-x}$) and BCY ($BaCe_{0.8}Y_{0.2}O_{3-x}$) were prepared by GTI and successfully tested in the new permeation unit.

During this reporting period, two different types of membranes, Eu-doped $SrCeO_3$ (SCE) and $SrCe_{0.95}Tm_{0.05}O_3$ (SCTm) provided by the University of Florida and the University of Cincinnati, respectively were tested in the high pressure permeation unit. The SCTm membrane, with a thickness of 1.7 mm, showed the highest hydrogen permeability among the perovskite membranes tested in this project so far. The hydrogen flux measured for the SCTm membrane was close to 0.8 cc/min/cm$^2$ at a hydrogen feed pressure of about 4 bar at 950$^{o}$C.

SEM and EDX analysis for the tested SCTm membrane showed a separate Ce-rich phase deposited along the grain boundaries in the region towards the feed side of the membrane. No such phase separation was observed towards the permeate side. Partial reduction of the SCTm perovskite material by the high pressure hydrogen, especially in the feed side of the membrane, was postulated to be the possible reason for the phase separation. Further investigation of the stability issue of the perovskite membrane is needed.

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## INTRODUCTION

The objective of this project is to develop a novel membrane reactor for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. This concept has the potential of significantly increasing the thermal efficiency of producing hydrogen, simplifying the processing steps and reducing the cost of hydrogen production from coal. The specific objective of the project is to determine the technical and economic feasibility of using the membrane reactor to produce hydrogen from coal. GTI and our project team (University of Cincinnati, University of Florida and American Electric Power (AEP)) have identified potential membranes (ceramic and metal) suitable for high temperature, high pressure, and harsh coal gas environments. The best performing membranes will be selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with other hydrogen production technologies from coal.

Our approach to membrane material screening and testing is to first identify the materials that have good thermal stability under the conditions of gasification temperatures. The candidate membranes are then evaluated for their hydrogen flux in a laboratory permeation unit. The acquired data will provide the basis for a preliminary membrane gasifier design, process development and economic analysis. In the next stage of material screening, chemical stability of the membranes with the syngas and its contaminants generated from coal gasification will be evaluated. The trade-off between the hydrogen permeability and chemical stability will be determined.

As coal gasification for hydrogen production occurs at temperatures above 900$^{o}$C and pressures above 20 atm, it is critically important to evaluate the hydrogen flux of the candidate membrane materials under these operational conditions. To this end, a high pressure/high temperature permeation unit has been constructed. The unit is capable of operating at temperatures and pressures up to 1100$^{o}$C and 60 atm respectively. The unit allows screening and testing of the membrane materials at more realistic gasification temperature and pressure conditions. Furthermore, it will be able to demonstrate much higher hydrogen flux from the membranes than what have been reported in the literature.

The mixed proton-electron conducting membrane of the perovskite has been identified as one of the candidate membranes for the membrane gasification reactor applications. The perovskite membrane is 100% selective to hydrogen at high temperatures, >600$^{o}$C. BCN ($BaCe_{0.8}Nd_{0.2}O_{3-x}$) and BCY ($BaCe_{0.8}Y_{0.2}O_{3-x}$) were first selected for evaluation because they were shown in the literature to have the highest proton conductivity among the perovskite materials. Several perovskite membranes based on the formulations of BCN and BCY were prepared by GTI and successfully tested in the new permeation unit, as reported in the previous quarters.

Europium (Eu) doped barium cerates and strontium cerates have been studied for their conductivity and hydrogen permeability [1,2,3]. Due to the large third ionization

potential of Eu, the bivalent cation, $Eu^{2+}$ is more stable than the trivalent cation, $Eu^{3+}$. Consequently, the Eu-doped perovskite can potentially have high electronic conductivity [2]. Indeed, the Eu-doped barium cerates have shown much higher hydrogen permeation flux than other dopants [1,3]. To further evaluate the advantages of Eu-doped perovskites, the powders form of Eu-doped strontium cerates prepared by the University of Florida were requested and were fabricated into membrane disks at GTI for the permeation testing.

The electrical conduction and hydrogen permeation of $SrCe_{0.95}Tm_{0.05}O_3$ (SCTm) have been studied by Qi and Lin [4]. SCTm actually showed high electronic conductivity in pure oxygen atmosphere despite the low ionization potential of Tm. Three SCTm membrane disks were obtained from the University of Cincinnati to evaluate the hydrogen permeation flux in the high pressure permeation unit. The tests were conducted covering a wide range of pressures, temperatures and the hydrogen feed compositions. The results are summarized in this report.

## EXECUTIVE SUMMARY

Two SCE membranes, which were made at GTI based on the powders supplied from Dr. Eric Wachsman of University of Florida were successfully tested in the high pressure permeation unit. One was with 10% Eu doping and the other was 20% Eu doping. The thickness of the membranes was about 0.3 - 0.4 mm. The measured hydrogen flux was about 0.34 STP cc/min/$cm^2$ at 6 bar and 950C with 100% hydrogen in the feed. No significant difference in the flux was observed between the two membranes with different Eu dopings.

The hydrogen flux for two membrane disks of SCTm provided by Professor Jerry Lin of University of Cincinnati were also successfully measured for a pressure range of 1 to 12 atm, a temperature range of 800 to 1010$^oC$ and various hydrogen compositions in the feed. The membrane test lasted for about 11 days, with the membrane kept under an inert gas environment during the nights and the weekends at a temperature of 900$^oC$ (1650 $^oF$) or 950$^oC$ (1750$^oF$). The highest hydrogen flux measured was close to 0.8 cc/min/$cm^2$ at a hydrogen feed pressure of about 4 bar at 950$^oC$. The SCTm membrane, taken into account of its thickness of 1.7 mm, showed the highest hydrogen permeability among the perovskite membranes tested in this project so far.

SEM and EDX analysis for the tested SCTm membrane showed a separate Ce-rich phase deposited along the grain boundaries in the region towards the feed side of the membrane. No such phase separation was observed towards the permeate side. Partial reduction of the SCTm perovskite material by the high pressure hydrogen, especially in the feed side of the membrane, was postulated to be the possible reason for the phase separation. The stability issues of the perovskite membrane material will need to be addressed in the next phase of the development program. Testing for the long term stability of the membranes under a hydrogen environment will need to be conducted.

## EXPERIMENTAL

### High Pressure Permeation Unit

The experimental apparatus and the procedure for measuring the hydrogen flux of the candidate membranes were described in the previous reports. The unit was designed to operate at temperatures up to 1100$^{o}$C and pressures to 60 atm for evaluation of disc membranes with a diameter of about 2 cm. The membrane disc was sealed to the test fixture following the same techniques as described in the previous reports.

Before testing hydrogen-permeation membranes in the high pressure unit, helium was introduced to the feed side of the membrane while nitrogen was used in the permeate side as a sweeping gas to check the leakage across the membrane or the sealing material. The permeate gas was sent to GC for analysis of its composition. Absence of helium in the permeate stream indicated good quality of the membrane and the seal. However, the minimum helium leakage rate that can be detected depends on the sensitivity of GC and the flow rate of the sweeping nitrogen. Previously, the GC used in our laboratory could only detect down to 0.3% of helium in the sweeping nitrogen stream. In this quarter, the volume of the GC sampling loop was increased so that the detecting limit was improved to 0.03%. The sweeping flow for the leak checking procedure was also reduced to about 80 cc/min, compared to about 200 cc/min used for the hydrogen permeation testing. Thus, the leakage rate could be quantified, typically less than 20% of the hydrogen permeation rate. The membrane sealing was also improved by raising the temperature to about 1100$^{o}$C to ensure adequate softening or melting of the glass component in the sealant before lowering the temperature to the range of the hydrogen permeation testing, 800 to 1010$^{o}$C.

### Membrane Samples

During this reporting period, two types of perovskite membranes were tested in the permeation unit. One was Eu-doped $SrCeO_3$ (SCE) membrane with the powders provided from Professor Eric Wachsman of University of Florida and the other was $SrCe_{0.95}Tm_{0.05}O_3$ (SCTm) membrane with the disks prepared by Professor Jerry Lin of University of Cincinnati.

Approximate 0.5 kilogram of Eu-doped $SrCeO_3$ powders prepared from the laboratory of Professor E. Wachsman were received in June 2004. Several membranes were fabricated from these powders by the tape casting method at GTI. Initially, to increase the membrane strength, two tapes were laminated together to form a membrane with a thickness of about 15 mils or 380 μ. Two samples were tested in the high pressure permeation unit. One failed the test due to the sealing problem. The other one, despite no leakage in the sealing, did not produce any hydrogen flux. A new batch of membranes made by the tape casting method without lamination, i.e. single tape, was prepared. Two SCE membranes made by the single tape method were successfully tested in the high pressure permeation unit. One was with 10% Eu doping (x=0.1, SCE-10) and the other

was 20% Eu doping (x=0.2, SCE-20). The thickness of the membranes was about 0.3 - 0.4 mm.

Three membrane disks of SCTm were received from Professor Jerry Lin of University of Cincinnati. These are pressed membrane disks with a diameter of about 2 cm and a thickness of about 1.7 mm. These disks have required perovskite structure for proton conduction based on XRD analysis. Two of the membrane samples were tested in the high pressure permeation unit. The first membrane test lasted for about 11 days, with the membrane kept under an inert gas environment during the nights and the weekends at a temperature of 900$^{o}$C (1650 $^{o}$F) or 950$^{o}$C (1750$^{o}$F). A leak test was conducted every weekday morning to ensure the integrity of the membrane as well as the seal before proceeding to the hydrogen permeation testing. The second membrane sample, which had the same composition and thickness as the first sample was tested with the objective of reproducing the data from the first membrane. The feed gases used for the hydrogen permeation testing were either pure hydrogen or mixture of hydrogen and helium with a flow rate between 600 cc/min to 1300 cc/min. The nitrogen sweeping rates were between 120 cc/min to 200 cc/min. The permeate side hydrogen mole fractions generally were in the order of 1%. The pressures ranged from 1 to 12 atm and the temperatures from 800 to 1010$^{o}$C.

## RESULTS AND DISCUSSION

SCE membrane

The measured hydrogen flux for the SCE-10 (10% Eu doping in $SrCeO_3$) were shown in Figure 1 under different nitrogen sweeping flows. The hydrogen flux appear to increase with the increasing sweeping flow rate. A high sweeping flow can eliminate or reduce the mass transfer resistance in the gas phase of the permeate side. An insufficient sweeping gas flow would create a concentration gradient in the gas phase next to the permeate side of the membrane. Therefore, the measured flux increases with the flow rate of the sweeping gas and reaches a constant value eventually. The hydrogen flux for this membrane of 0.4 mm thickness is about 0.35 STP cc/min/cm$^2$ at 6 bar and 900$^{o}$C with 100% hydrogen in the feed. The hydrogen flux of the SCE-1 membrane at 12 bar and 900$^{o}$C with 100% hydrogen in the feed was also measured at 0.22 cc/min/cm$^2$, which is lower than the flux at 6 bar. (see discussion below for Figure 2)

Figure 2 is the hydrogen flux for the SCE-20 membrane at three different pressures for a hydrogen feed of 100% at 950$^{o}$C. The hydrogen flux goes through a maximum with the hydrogen feed pressure. It is not clear why the hydrogen flux decreases after 4 atm of the hydrogen feed pressure. Previous data with the BCN membranes show that the hydrogen fluxes reach a constant value after about 6 atm. Presumably, this could be due to the effect of hydrogen pressure on the proton/electron conductivity.

The hydrogen flux for the SCE-20 membrane is about 0.38 STP cc/min/cm$^2$ at 6 bar and 950$^{o}$C with 100% hydrogen in the feed. No significant difference in the flux was

observed between the two membranes with the different Eu dopings. The fluxes generally are lower than the BCN membranes reported previously. However, the fluxes, after extrapolating to the ambient pressure, are much higher than the literature values [2]. The fluxes reported by Song et al. [2] are in the order of 0.004 cc/cm$^2$/min, which are one order of magnitude lower than the typical proton-electronic conducting perovskites.

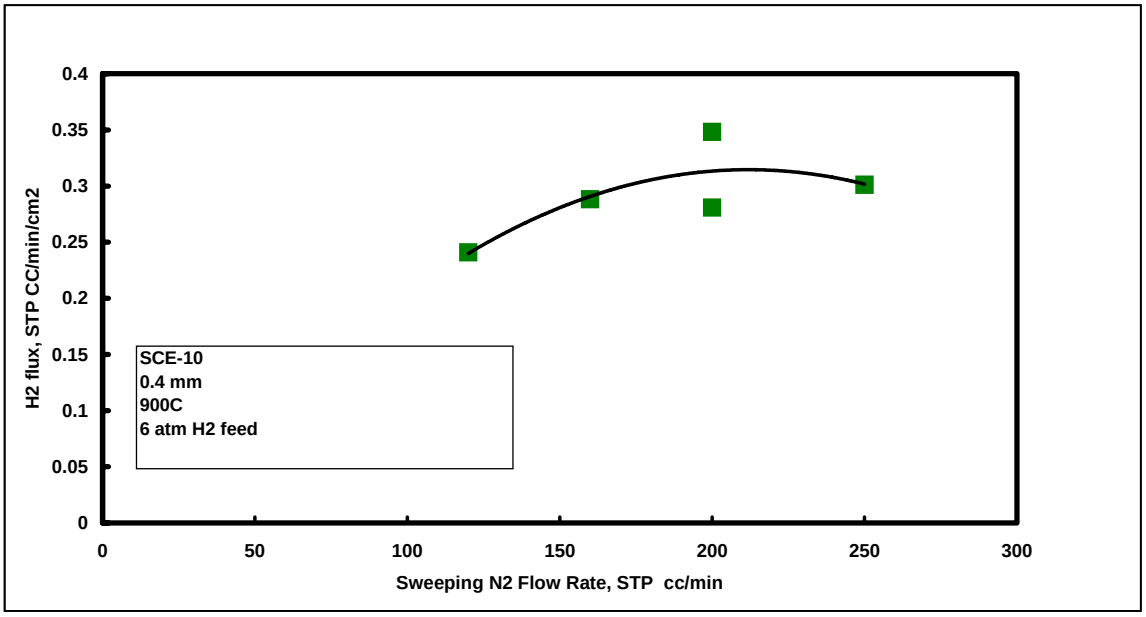



**Figure 1. Hydrogen permeation flux for SCE-10 membrane measured from high-pressure permeation unit**

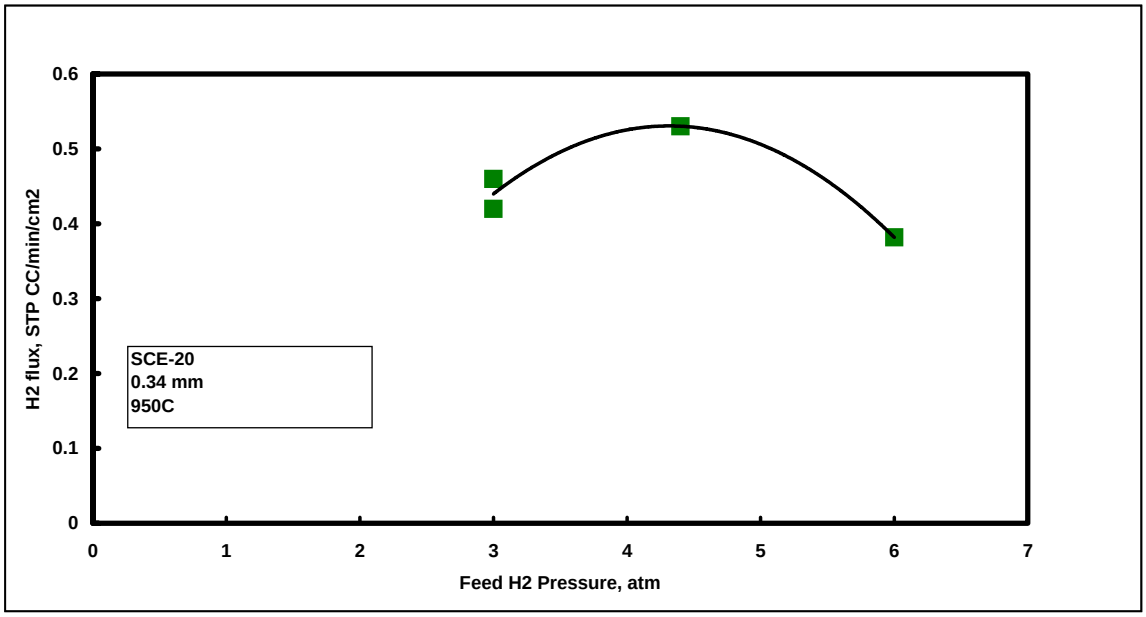



**Figure 2. Hydrogen permeation flux for SCE-20 membrane measured from high-pressure permeation unit**

SCTm membrane

The hydrogen permeation results for the SCTm membrane at 950°C (~1750°F) are summarized in Figure 3 for the different hydrogen feed partial pressures. The hydrogen flux increases with the increasing feed pressure up to about 5 atm and then decreases with the pressure, as shown in Figure 3 by the curve with 100% $H_2$. With 60% hydrogen in the feed (balance of helium), the hydrogen flux still goes through a maximum with respect to the hydrogen partial pressure in the feed, as shown by the curve with 60% H2 (triangle points). Also shown in the figure is the effect of the hydrogen compositions in the feed on the flux at 8.14 atm. The hydrogen compositions in the feed were 20, 40, 60, 80 and 100% for this curve with the diamond points. As expected, the flux increases with the increasing composition or the partial pressure of hydrogen in the feed. Similar effect of the hydrogen compositions at 1 atm pressure is shown in the same figure. The hydrogen compositions are 100%, 60% and 20% at 1 atm for the curve with the open circles. The measured hydrogen flux with 20% hydrogen in the feed at 1 atm is also close to the literature data reported by Qi and Lin [1].

The second SCTm membrane was tested with a pure hydrogen feed at 950°C and various pressures. The hydrogen flux measured from this membrane are also shown in Figure 3. As can be seen, some of the data from the first membrane can be reproduced by the second membrane.

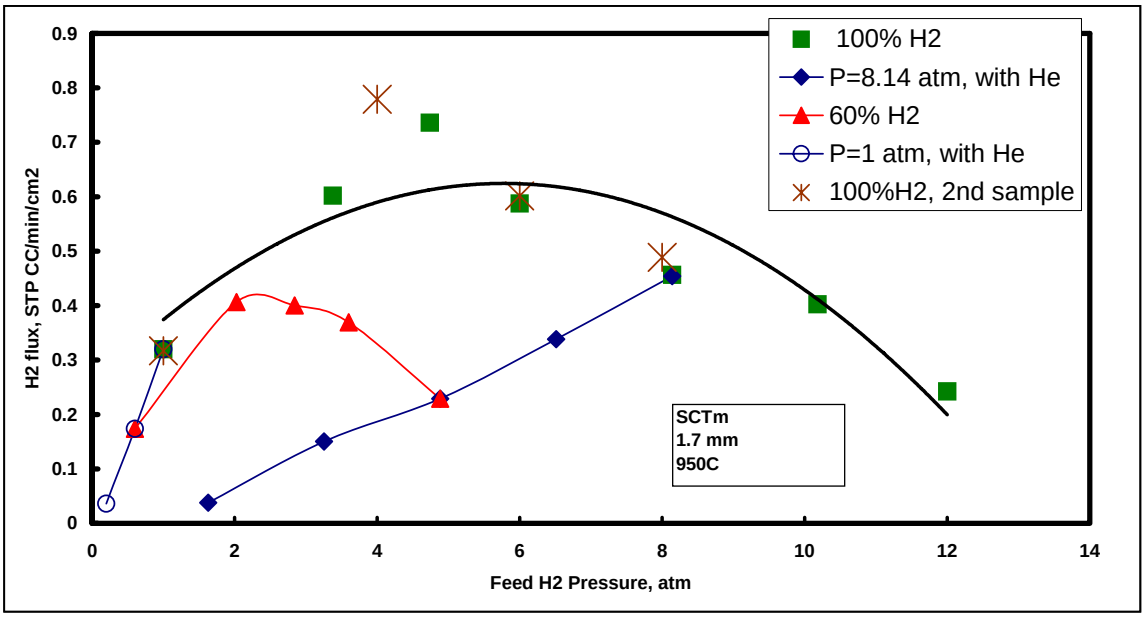



**Figure 3. Hydrogen flux for the SCTm membrane at different $H_2$ partial pressures**

If the membrane thickness is taken into consideration, the SCTm membrane (thickness 1.7 mm) shows much higher flux than the SCE membranes (thickness 0.3-0.4 mm). The

fluxes are also higher than the BCN membranes reported previously. The SCTm membrane will be investigated further.

Additional data for the temperature dependency of the hydrogen flux for the SCTm membrane are shown in Figure 4 with 100% hydrogen in the feed at a pressure of 4.7 bar. The temperature varied between 800 and 1010$^{o}$C. As expected, the hydrogen flux increases with the increasing temperature. The calculated activation energy is about 45 Kcal/mole.

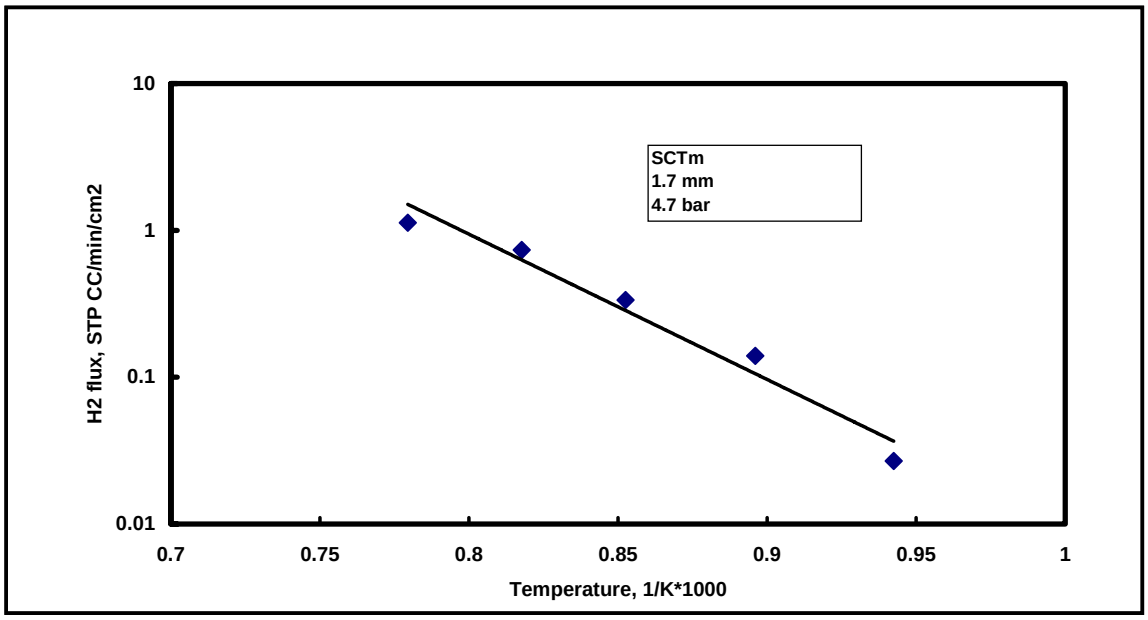



**Figure 4. Hydrogen flux for the SCTm membrane at different temperatures**

SEM and EDX Analysis of SCTm Membrane

The SCTm membrane after the permeation testing was removed from the test fixture and analyzed by micrography. The sample was fractured near the center and one piece was polished in the area of the cross section. The polished cross section was examined under a scanning microscope (SEM). Figure 5 is a SEM micrograph showing the entire cross section. There is a significant population of black dots in the picture. They are identified as pores as will be shown later.

A representative area near the feed side of the sample was magnified to 500X. Two connecting pictures, shown in Figure 6 were taken to include different features. The pores do not appear to be connected together, but look more like isolated islands. However, some cracks are visible, especially in the picture of the right hand side. The cracks also propagate almost to the entire picture. Not all cracks initiates from the surface as there are also cracks running parallel to the surface (near the bottom of the right

picture). The cracks may have been caused by the force applied to remove the disk from the membrane tube after the permeation testing.

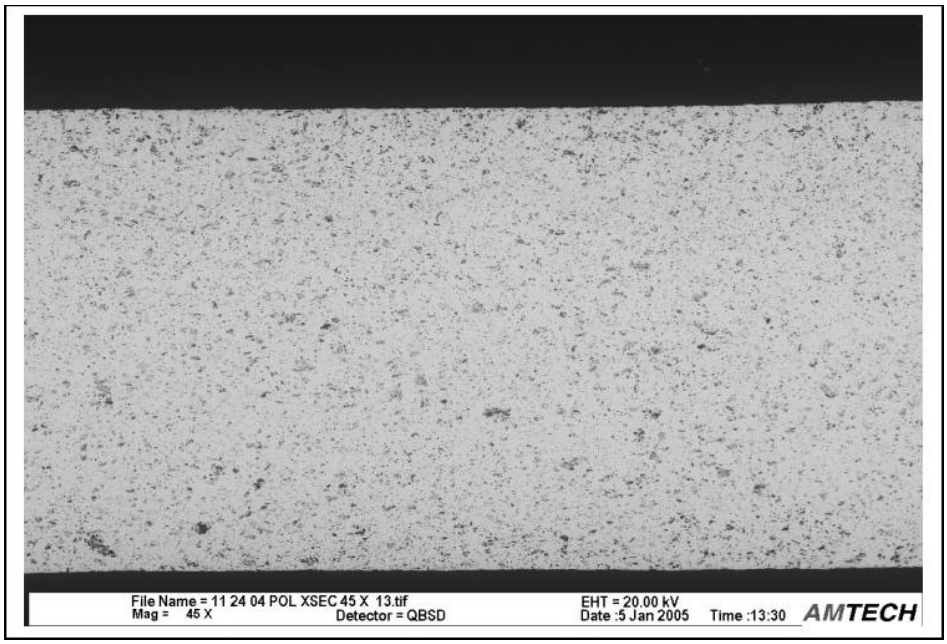



**Figure 5. Polished cross section of the tested SCTm membrane with the feed side at the top and the permeate side at the bottom**

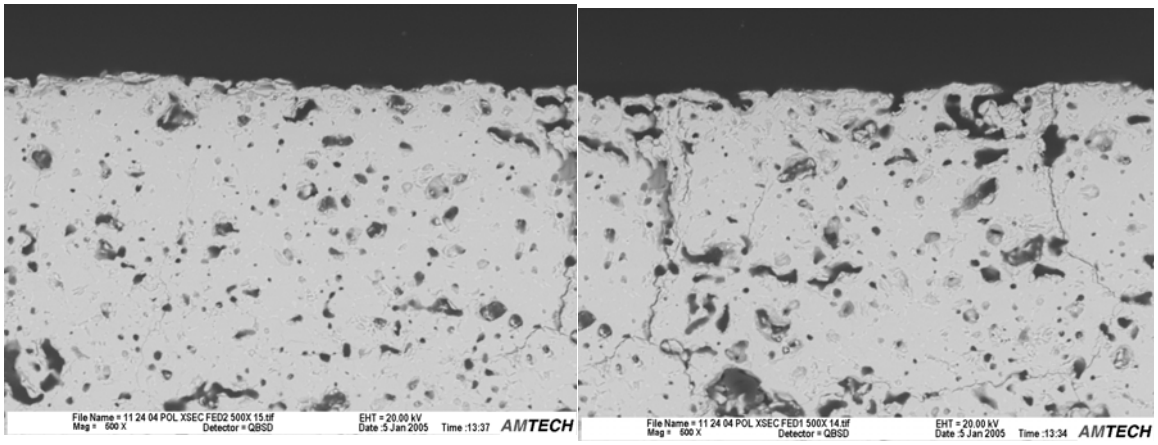



**Figure 6. Two connecting areas for the feed side of the SCTm membrane magnified at 500X**

A crack-free area was further examined at 2000X to visualize the features of the microstructure. It was observed that in addition to the empty pores, light colored material formed between grains (see Figure 7). To detect the elements present in the light colored areas, Energy Dispersive Spectra (EDS) was used with the electron beam pointed at the grain bulk and the grain boundary regions separately. The relative concentration of the elements between the grain bulk and the grain boundary areas can then be determined. The EDS spectra of the two areas are shown in Figure 8. As shown, the light colored material along the grain boundary is rich in Ce (Figure 8-a, top) while the bulk is richer in Sr (Figure 8-b, bottom). Presumably, cerium oxide could be separated from the perovskite structure and deposited along the grain boundaries.

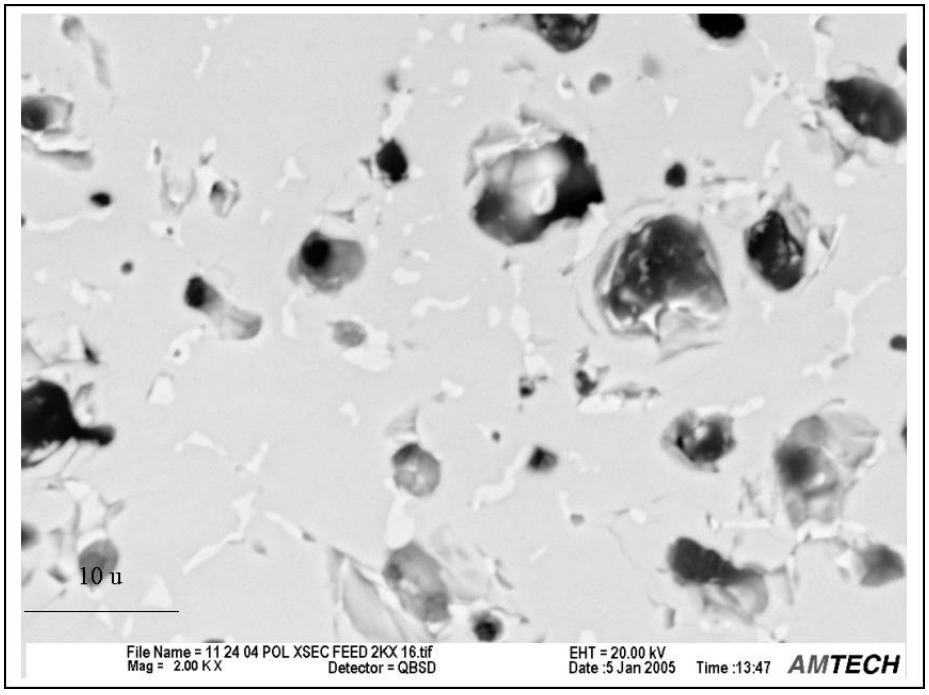
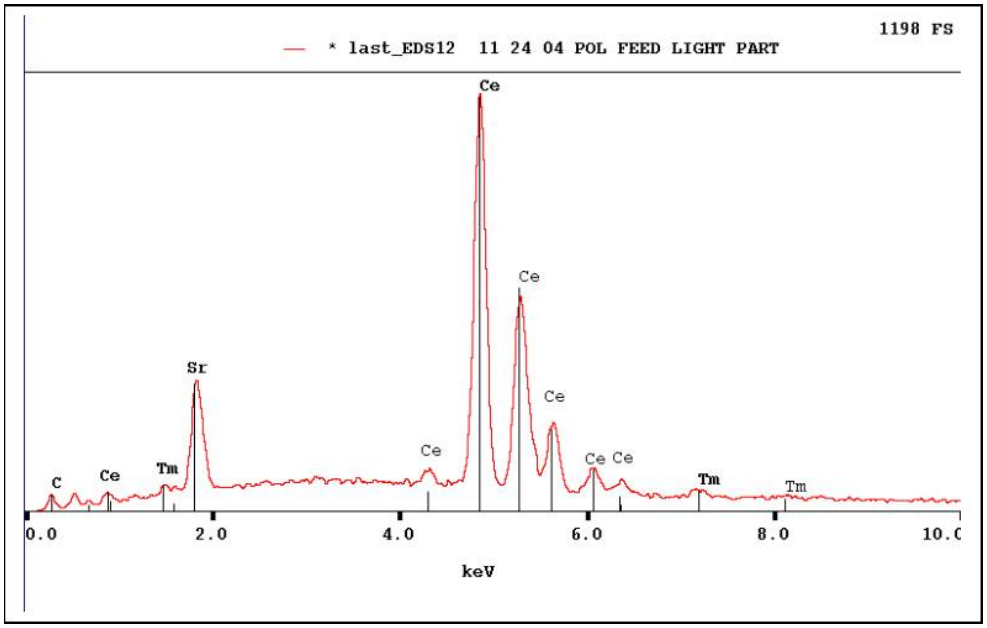



**Figure 7. 2000X Magnification of SCTm membrane near the feed side showing light colored grain boundaries under a slight back scattered mode**

**(a)**




**(b)**

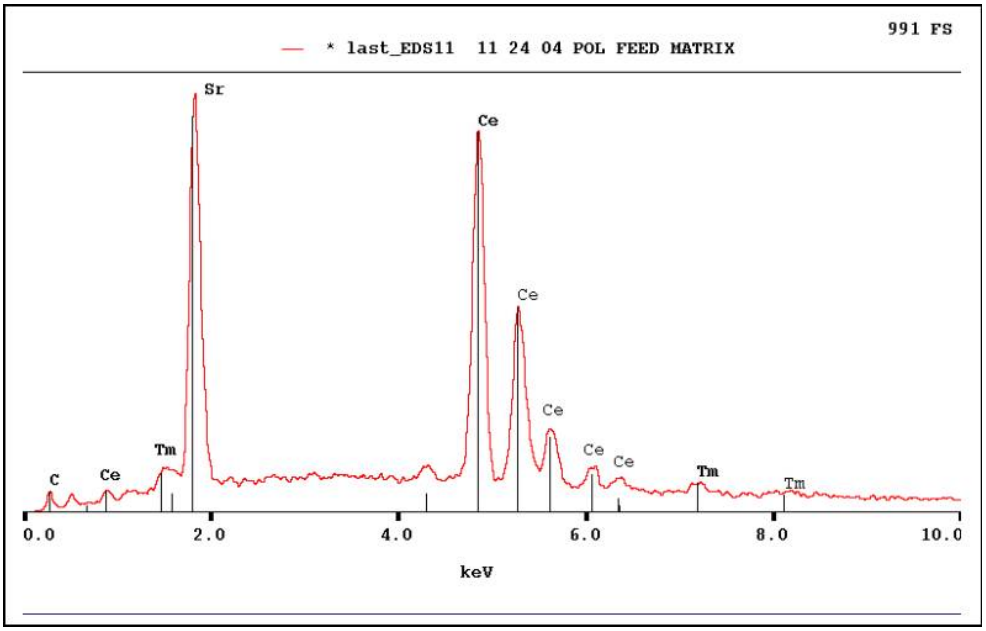



**Figure 8. EDX pattern of (a) the light colored region, and (b) the background region, from the SEM micrograph shown in Figure 7**

The interior of the sample was also examined by SEM. As in the feed side of the membrane, light colored materials appeared between the grains. No significant differences were observed between this interior area and the feed side of the membrane. The SEM graphs are similar to the Figures 6 and 7 and are not shown here.

An area near the permeate surface was also examined. Micrographs at 500X are shown in Figure 9. It appears to have a larger population of the pores than the area near the feed surface (compare Figure 6 and 9). Micrograph at 2000X of two connecting areas is shown in Figure 10. In contrast to the area near the feed side in Figure 7, the solid material seems homogeneous and no phase separation is evident. An EDS spectrum of the material near the permeate side is shown Figure 11. It shows that the area is rich in Sr, similar to the bulk material of the preceding areas in the feed side and the interior of the membrane.

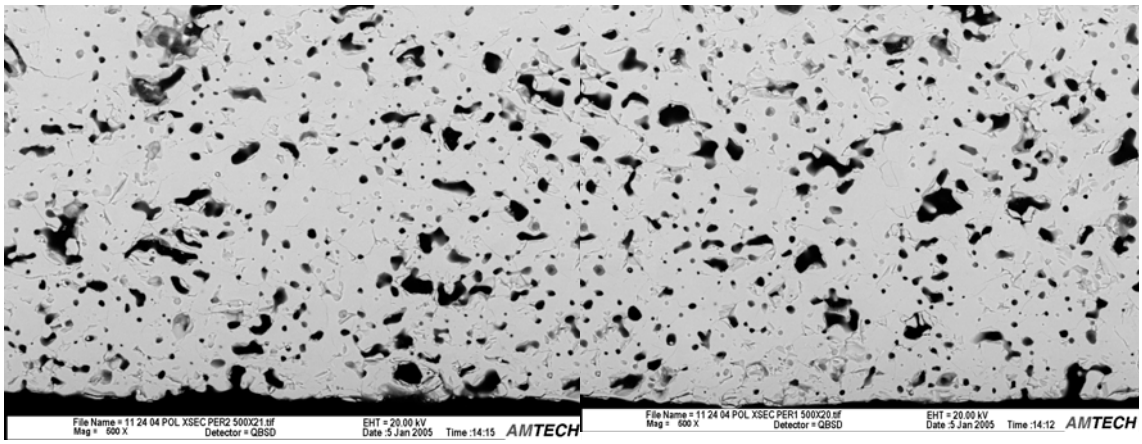



**Figure 9. Two connecting areas for the permeate side of the SCTm membrane magnified at 500X**

From the above SEM and EDX analysis on the tested SCTm membrane, there appears to have a phase separation for the perovskite structure, especially in the feed side of the membrane. Because the feed side of the membrane had been encountered with pure hydrogen at pressures during the permeation testing, the perovskite could have been partially reduced by hydrogen to cause the phase separation. The phase separation was not visibly seen in the SEM graph for the permeate side of the membrane, perhaps due to the low hydrogen partial pressure in the permeate side. The stability issues of the perovskite membrane material will need to be addressed in the next phase of the development program. Testing for the long term stability of the membranes under a hydrogen environment will need to be conducted.

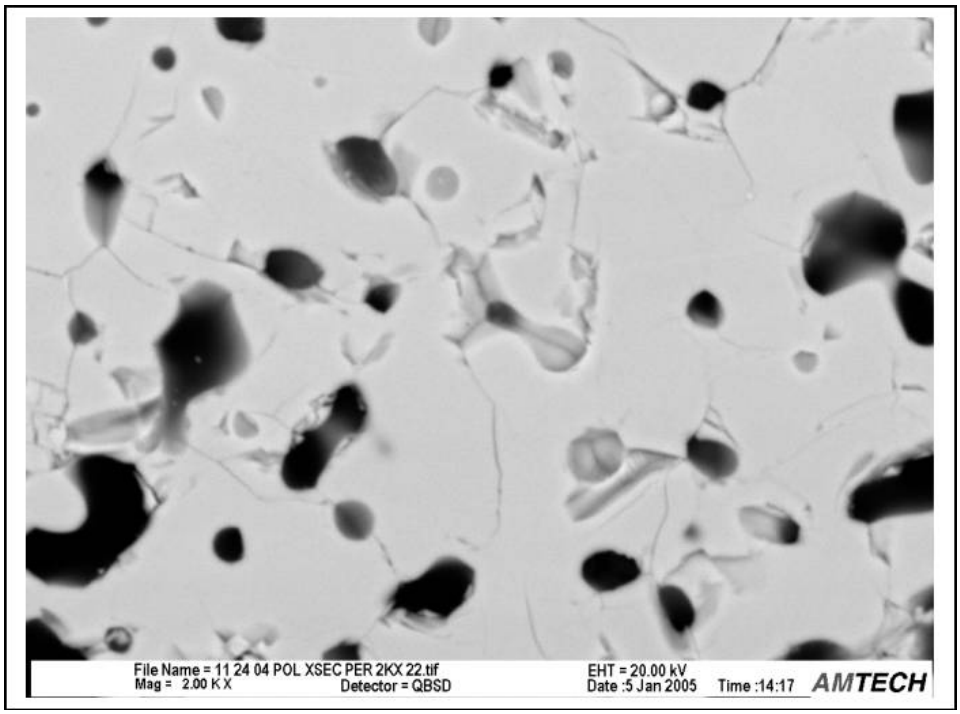



**Figure 10. 2000X Magnification of SCTm membrane near the permeate side showing little presence of light colored areas**

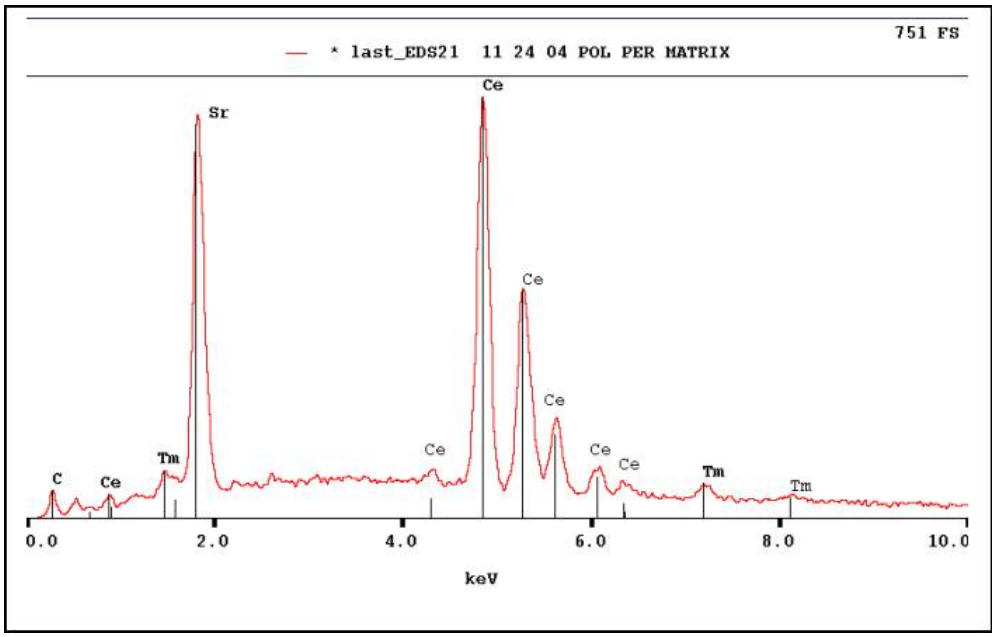



**Figure 11. EDX pattern of the bulk region near the permeate side**

## CONCLUSION

Two SCE membranes, which were made at GTI based on the powders supplied from Dr. Eric Wachsman of University of Florida were successfully tested in the high pressure permeation unit. One was with 10% Eu doping and the other was 20% Eu doping. The thickness of the membranes was about 0.3 - 0.4 mm. The measured hydrogen flux was about 0.34 STP cc/min/$cm^2$ at 6 bar and 950C with 100% hydrogen in the feed. No significant difference in the flux was observed between the two membranes with different Eu dopings.

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## PLAN FOR NEXT QUARTER

- Hydrogen permeation testing for the perovskite membranes will be continued for the supported ultra-thin membranes prepared by the tape casting technique.
- Conduct hydrogen permeation testing of the perovskite membranes for an extended period of time (more than 100 hours in a hydrogen environment)
- Complete conceptual design of membrane gasifier configuration for a plant of 1000 TPD coal. Design will be based on initial hydrogen permeation data and modeling approach.
- Conduct literature review to identify the approaches for addressing chemical stability issues of perovskite membrane.

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