ESRF	**Experiment title:** Towards hydrogen economy: SAXS /WAXS study of microporosity and microstructure of amorphous SiBCN membranes for hydrogen purification	**Experiment number**: MA-698
Beamline: ID 02	**Date of experiment**: from: 12 June 2009 to: 15 June 2009	**Date of report**: 1 March 2010
Shifts: 9	**Local contact(s)**: Dr. Peter Boesecke	*Received at ESRF:*

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Report:

Objectives

Aim of our experiment was to investigate the presence of microporosity (pore diameter < 2 nm) in amorphous SiBCN membranes coated on supports with different carbon and boron content using SAXS/ WAXS.

Growing interest in the use of hydrogen as main fuel has increased the need for pure hydrogen production and purification. There are several by-products (CO, H_2O, CO_2 …) associated with the production of hydrogen. Therefore, separation of hydrogen from other gases is an important step in the hydrogen production process [1]. The amorphous polymer-derived SiBCN membranes are expected to have great potential for high temperature H_2 purification [1, 2]. They are attractive due to their chemical and thermal stability, which provides the possibility to regenerate and decontaminate them at high temperatures [3]. Because of limitations of gas adsorption methods, SAXS will be used to determine microporosity [4, 5] of amorphous SiBCN materials.

Experimental

Small angle X-ray scattering (SAXS) was performed at beamline ID 02, ESRF with a sample-to-detector distance of 1.101 m. Powder unsupported Si-B-C-N membranes were introduced into quartz capillary tubes of 1 mm diameter. The optimal intensity of the radiation were determined with different exposure times. Empty capillary tubes were also measured for normalization purposes. The measured samples were labeled as “Hexa_” followed by the pyrolysis temperature and heating rate. The sample labeled ‘Hexa_1000C_100K/h’ is the sample pyrolyzed at 1000 ºC with a heating tate of 100 K/h.

Results

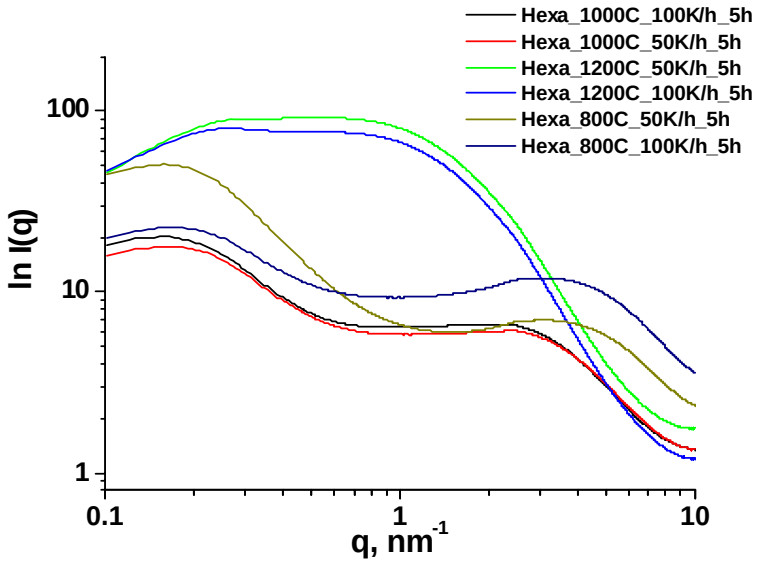

Figure 1. SAXS curves of the Si-B-C-N membranes pyrolysed at different temperatues.

Figure 1 shows small angle x-ray scattering curves of the samples after intensity normalization. Scattering curves of samples clearly show evolution of interface (in porod region) that gives rise to scattering for the samples pyrolysed at 800 ºC and 1000 ºC. It confirms presence of microporosity in the unsupported membranes. Porod behaviour was shifted to lower q region as pyrolysis temperature was increased from 800 to 1000 ºC. This behaviour clearly indicates increased in pore-size for membranes obtained at 1000 ºC compared to 800 ºC. At 1200 ºC, no such scattering was observed. This indicates membrane loses it microporosity at 1200 ºC.

SAXS data obtained after subtracting background and other normalization process were analyzed using Igor Pro/ Irena package. Following parameters were used for calculating pore size distribution:

- Distribution parameter: minimum diameter- 4 Å , maximum diameter- 100 Å.
- Shape model: Cylindrical AR (Aspect ratio), AR ~ 900 were used
- Method: IPG/TNNLS (Total Non-negative least square) method
- NNLS approach parameter: 0.56, Approach parameter is the step-size which is made in each step towards calculated ideal solution.

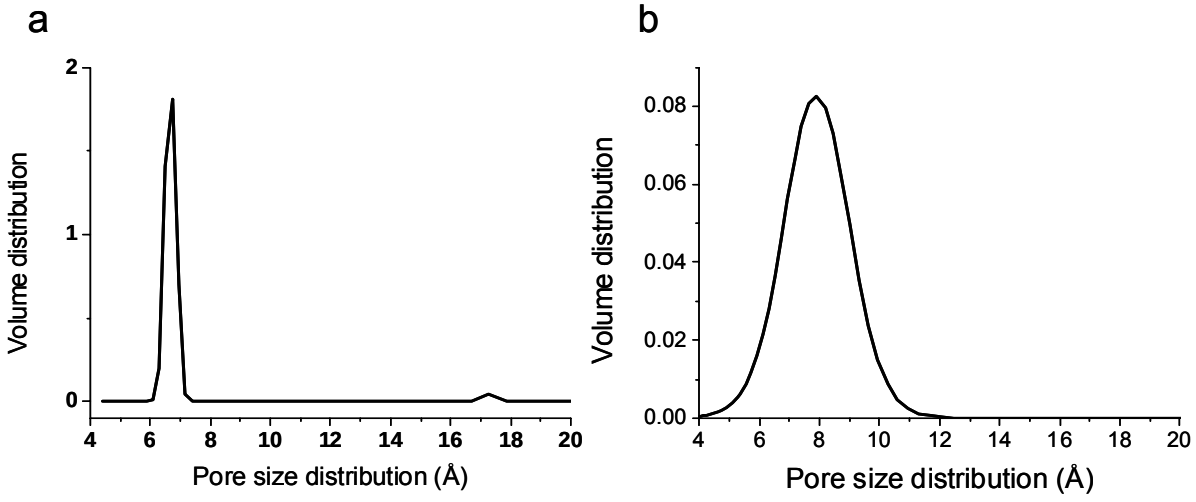

Figure 2. Pore size distribution of unsupported Si-B-C-N membrane pyrolyzed at (a) 800 ºC_100 K/h and, (b) 1000 ºC_100 K/h using Igor Pro/ Irena package.

Processed results for two of the unsupported Si-B-C-N membranes using Igor Pro/ Irena package are shown in figure 2. Pore size of unsupported membranes pyrolysed at 800 ºC and 1000 ºC were found to be 6.7 Å and 7.8 Å respectively. Comparing these results with those obatained using N_2 sorption analysis (Figure 3) shows pore size distributions determined by the small angle x-ray scattering technique agree with that of the commonly used gas adsorption technique.

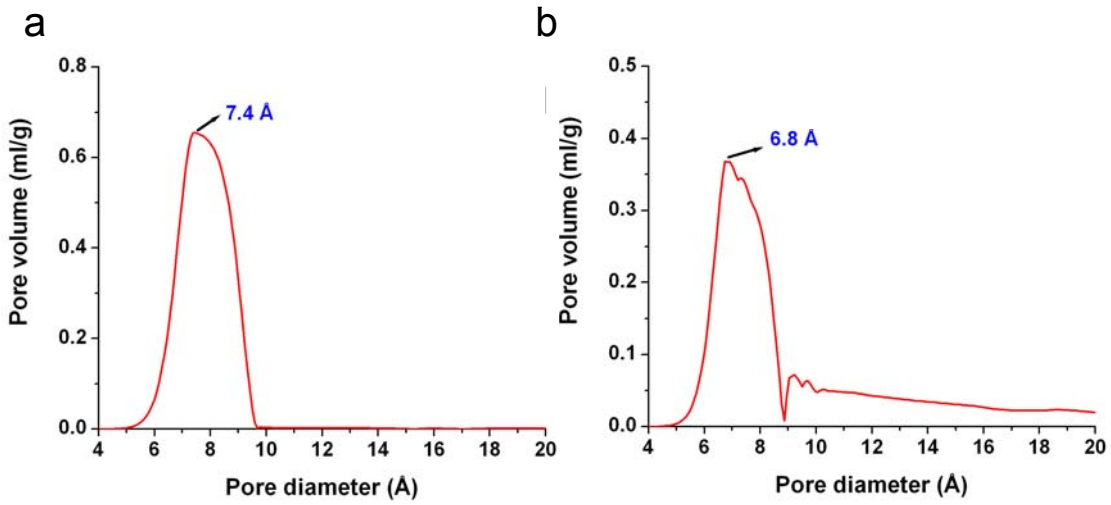

Figure 3. Pore size distribution of Si-B-C-N membrane on the (a) porous α-alumina support, (b) porous α-alumina support with mesoporous γ-alumina intermediate layer using nitrogen gas sorption method.

The manuscript preparation is in progress.

References

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