

CERAMIC MEMBRANES FOR
HYDROGEN PRODUCTION FROM COAL

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Abstract

A technique was developed to extrude thin glass tubes from a glass-polyethersulfone-solvent (NMP) paste with a glass to polymer weight ratio of about 8. The extrudates were gelled in water and heat treated at 800-950°C to remove the polymer and sinter the particles to a dense glass structure. Subsequently, the tubes were leached in hot water to remove the soluble phase formed by phase separation during cooling. The tubes were characterized by XRD, SEM, and permeation measurements. SEM examination indicated that during leaching the glass developed pores of about 100 nm size. Permeation measurements showed lack of separation selectivity consistent with the pore size observed in SEM.

1. Introduction

Project Objectives

The project objectives were to develop hydrogen permselective silica membranes suitable for integration with water gas shift (WGS) reactors for production of pure hydrogen from coal or other fuels. Specific targets were membrane permeance above 10 MPU (1 MPU = 10^{-8} mol/m²-s-Pa) and H₂:CO₂ separation factor above 250 under operating conditions of a WGS reactor.

Summary of Work in the Previous Period

The work performed earlier was described in the previous annual report. Briefly, silica membranes were prepared starting with α -alumina tubes of pore size approximately 0.18 μ m and growing hydrothermally a silicalite layer inside the alumina pores. This modified support had pores of 0.55 nm (the channel size of silicalite) but also contained defects due to incomplete zeolite growth. This modified support was subsequently subjected to chemical vapor deposition involving alternate exposures to silicon tetrachloride vapor and water vapor at 400-

450°C to form the final silica membrane. Membrane characterization and permeation testing led to the following conclusions:

(i) CVD by half reactions of silicon tetrachloride and water vapor at temperatures 400, and 450°C did not produce a silica layer but introduced silica species into the zeolitic channels and narrowed these channels.

(ii) The narrowing of the zeolitic channels resulted in a gradual increase of the H₂:N₂ permeance ratio at 150°C from about 3 before CVD to 100-200 after 25 cycles of CVD.

The H₂:CO₂ ratio was lower, about 30. These properties are the direct consequence of the fact that separation takes place by the narrowed zeolitic channels rather than by an external silica layer.

(iii) Using silicalite membranes with fewer or smaller defects would provide higher selectivities but the useful temperature range would remain below 250°C.

General Approach

In view of the results of the previous annual period the approach based on silicalite/alumina supports was suspended. The effort was redirected to using porous glass supports of sufficiently high permeance. Two types of such supports were considered. One was alumina tubes coated with a thin porous glass layer. The other was porous glass tubes of low thickness or asymmetric structure and surface pore diameter 2-5 nm. In previous work in our laboratory we had difficulty preparing glass-coated alumina supports because of the reaction between glass and alumina during the high temperature processing. This reaction altered the composition of the glass so that the resulting layer was not suitable any more for the subsequent steps of phase separation and leaching. In the present project we pursued the second type of glass supports, namely thin porous glass tubes of small diameter prepared using a novel extrusion technique.

Thin ceramic tubes (alumina, zirconia etc) have been previously made by extrusion of a paste of inorganic material and a polymer or some other binder (Smid et al., 1996; Terpstra et al., 1998), or by extrusion of a particle-polymer-solvent mixture followed by gelation (phase-inversion) in a nonsolvent (Dobo and Graham; 1979; Lee and Kim, 1991; Luyten et al., 2000; Liu and Li, 2003). In both techniques, the tube precursors containing the ceramic powder and the polymer are heat-treated in air to pyrolyze the polymer and burn out the residual carbon. The ceramic particles are then sintered to a dense or porous structure.

In contrast to ceramic tubes, very thin glass tubes (hollow fibers) have been made by extrusion of the *melt* (Schnabel et al., 1977; Hammel, 1989; Kuraoka et al., 2002) which, however, requires special equipment. In this work it was decided to apply extrusion from a suspension of glass particles, rather than from the melt, using a home-made extrusion apparatus. After extrusion and heat treatment the nonporous glass tubes are leached in acid to generate connected porosity.

2. Experimental

2.1. Materials

A glass of composition 9.1% Na₂O–29.7% B₂O₃–61.2% SiO₂ (by weight) was supplied by Corning Inc. in the form of chips approximately 0.5 mm thick. Glass chips were crushed and ball-milled to a glass powder which was used as the starting glass membrane material. Polyethersulfone (PESf) [Radel A-300, Ameco Performance, USA], and N-methyl-2-pyrrolidone (NMP) [Synthesis Grade, Merck] were used for preparing the starting suspension. Polyvinylpyrrolidone (PVP, K90) [GAF[®] ISP Technologies, Inc. M_w = 630,000] was used as an additive. Tap water was used as both the internal and external gelation medium (nonsolvent).

2.2. Tube Preparation

PESf was slowly added to NMP under stirring to form the polymer solution. The required quantity of NMP was introduced in one-liter wide-neck reaction flask and the PESf was slowly added to form the polymer solution. After the polymer solution was formed, a given amount of glass powder was added and the mixture was stirred for 24 hours to ensure that all the glass particles were dispersed uniformly in the polymer solution. PVP was also introduced into the solution as an additive to modulate its viscosity. Finally, the polymer solution was degassed at the room temperature. The degassed paste containing the glass powder was transferred to a stainless steel reservoir and pressurized with nitrogen to 40 psig. Extrusion was carried out through a *tube-in-orifice spinneret* with orifice diameter and inner diameter 2.5 and 0.72 mm respectively. The extruded tubes emerging from the spinneret at 10 cm/min were passed through an air gap of 4 cm and immersed in a water bath to complete gelation.

After thorough washing in water, the gelled tubes were pyrolyzed in an electrical furnace at 800-950°C for several hours to decompose and burn out the polymer and sinter the glass particles. For that purpose an alumina tube of 3.5 mm ID, 5 mm OD and 20 cm length was used as the sample holder into which one glass-polymer tube of approximately 8 cm length was inserted near the plugged end. The tube was then inserted in a furnace so that the precursor tube was located in the central, relatively uniform temperature section. The open end of the alumina sample holder protruded 8 cm outside of the furnace and was open to the atmosphere. The details of the heat treatment are crucial to the properties of the final tube. When the glass-polymer precursor is inserted in a *preheated furnace*, heating is relatively rapid so that the polymer is converted to relatively unreactive carbon before oxidation can be completed. By inserting the sample in the furnace at room temperature and

heating to the final temperature at a specified heating rate it is possible to oxidize the polymer residue before sintering of the glass particles takes place.

After heat treatment, the glass tubes were leached in aqueous acid or in hot water at a specified temperature and for a specified time to generate connected porosity. The conditions of leaching are also important to the final tube properties.

2.3. Tube Characterization

The glass-polymer tubes were examined with a scanning electron microscope (JEOL JSM-5600 and LEO 1550 VP field emission SEM). After immersion in liquid nitrogen for about 5 minutes these precursor tubes were slowly flexed until a clear cross-sectional fracture occurred. The tubes were subsequently gold-coated using sputter coating under vacuum. In the case of the heat treated tubes, the clear cross-sectional fracture was obtained by direct breaking. SEM micrographs of tube surface and cross-section were taken at various magnifications.

The presence of any crystalline phases in the original glass powder and the crashed heat-treated glass samples was examined using an X-ray diffractometer. The permeance of several gases was measured at several stages of tube preparation, glass-polymer precursor, heat-treated tube, and leached tube. For this purpose one end of the tube was sealed by a quick-setting epoxy resin and the tube was then placed within a larger concentric steel tube. Nitrogen and other gases were passed at about 2 bars through the annulus while the permeate collected at the ID side was conducted to a bubble flowmeter. The permeance was calculated from the tube dimensions, permeate flow rate, and feed pressure by the equation:

$$J = \frac{Q}{\pi L D \Delta p}$$

where J , Q , D , L and Δp are the gas permeance ($\text{mol/m}^2\cdot\text{Pa}\cdot\text{s}$), permeate flowrate (mol/s), fiber OD (m), length (m), and partial pressure difference across the fiber wall (Pa), respectively.

3. Results and Discussion

After relatively mild heat treatment the glass particles do not undergo densification and the resulting tubes have micron-sized pores and are not gas-tight even before leaching. By using more severe heat treatment conditions, the smaller pores near the tube surface may be partially or completely eliminated leading to a dense structure. Our results indicate that dense tubes can be prepared using the following conditions:

- (i) The starting suspension contains glass to polymer weight ratio of 8.
- (ii) The glass-polymer tubes are heated at $800\text{ }^\circ\text{C}$ to $930\text{ }^\circ\text{C}$ for 5 to 15 hrs.

Following the heat treatment the densified glass tubes were leached in aqueous acid solution to generate connected porosity. It was found that glass tubes leached in aqueous acid solution (i.e., HCl, HNO_3) had low mechanical strength and were usually broken during leaching. When, instead, leaching was carried out using hot water, the mechanical strength of the leached tubes improved greatly. Figures 1 and 2 show SEM micrographs of a glass tube cross section and OD surface before leaching. The cross section indicates complete fusion of the glass particles. Figure 3 shows SEM of the glass surface after leaching. The cross section is covered with pits of about 100 nm diameter, suggesting that the actual pore size is also about 100 nm. In the traditional Vycor process which produces tubes by melt extrusion, the pores that result from leaching have usually about 4.5 nm mean diameter. The major cause for the larger pore size obtained in this project may be facile phase

separation resulting in domains of about 100 nm size. A likely reason for the facile phase separation is absence of certain components like ZrO_2 in the initial glass composition. These components increase viscosity and retard phase separation. Future work should focus on the effect of additives on phase separation and the resulting pore size.

Figure 4 is a lower magnification SEM of the cross section of a tube before leaching. The micrograph shows voids as large as 20 μm in the interior of the cross section but very few of these voids reach the tube surface. SEM observations show that these large voids are generated during gelation by complex diffusion and phase separation mechanisms similar to those encountered in the preparation of polymeric membranes. The presence of large particles in the initial glass powder may also contribute to these inhomogeneities. The glass powder was prepared by the traditional ball-milling method resulting in a wide size distribution including particles on the order of 10 μm . Presence of such large particles may hinder complete densification during heat treatment resulting in large size defects. Incomplete densification may also be responsible to the loss of mechanical strength upon leaching. .

Table 1 shows the gas permeation and ideal selectivity factors for glass tubes prepared under different heat treatment conditions. In all cases the tubes were leached in boiling water for 24 hours. The lack of separation selectivity shown in Table 1 indicates transport in the Transition (viscous-Knudsen) or viscous flow regimes consistent with the pore size observed in Figs. 3 and 4.

Table 1 Gas permeation and ideal selectivities for SBS glass membranes

Samples (Sint. Tem.)	Permeance (10^{-6} mol/m ² sPa) (1atm)												Selectivity					
	Room Temperature (23°C)						105°C						Room Temperature			105°C		
	H ₂	He	N ₂	CO ₂	nC ₄	iC ₄	H ₂	He	N ₂	CO ₂	nC ₄	iC ₄	He/ N ₂	N ₂ / CO ₂	iC ₄ / nC ₄	He/ N ₂	N ₂ / CO ₂	iC ₄ / nC ₄
800°C-a	30.20	19.00	11.2	11.07	15.68	15.36	21.62	13.90	8.00	7.40	8.43	9.01	1.70	1.01	1.02	1.74	1.08	0.93
800°C-b	25.02	14.00	9.83	9.81	13.98	13.44	14.2	8.96	5.55	5.35	8.13	8.26	1.42	1.002	1.04	1.61	1.04	0.98
850°C	2.88	2.02	0.97	0.89	1.37	1.13	-	1.67	0.78	0.65	0.67	0.72	2.09	1.09	1.21	2.13	1.21	0.92
900°C-a	18.8	11.5	6.53	7.1	12.0	11.16	-	0.93	5.24	5.02	7.0	7.18	1.76	0.91	1.08	1.72	1.04	0.97
900°C-b	13.70	5.58	4.86	4.61	-	-	-	-	-	-	-	-	1.76	1.05	-	-	-	-
930°C-a	31.90	20.96	11.4	10.60	20.29	18.88	134.97	98.41	29.98	28.61	25.31	23.69	1.84	1.08	1.07	3.28	1.05	1.07
930°C-b	8.31	6.07	2.98	2.80	4.23	3.96	15.44	8.32	5.42	4.36	5.60	4.94	2.04	1.06	1.07	1.54	1.24	1.13
930°C-c	29.93	19.41	10.50	10.08	-	-	-	-	-	-	-	-	1.84	1.04	-	-	-	-

4. Conclusions

An extrusion technique was developed for preparing glass tubes on the order of 2 mm OD and 0.25-0.5 mm thickness. After heat treatment and leaching these tubes developed pores of approximately 100 nm size resulting from rapid phase separation of the glass during cooling and solidification. Some glass tubes contained voids 10-20 μ m size formed during gelation of the extruded glass-polymer tubes. The presence of large particles in the mixture is a contributing factor to the preservation of these large voids, but it is not certain that the large voids penetrate through the tube surface providing alternate transport pathways. Permeation measurements indicate transport in the Knudsen or viscous flow regimes resulting in very low separation selectivity. Achieving separation selectivity requires changes in the glass composition to retard phase separation, and use of finer glass particles to eliminate inhomogeneities in the glass-polymer suspension.

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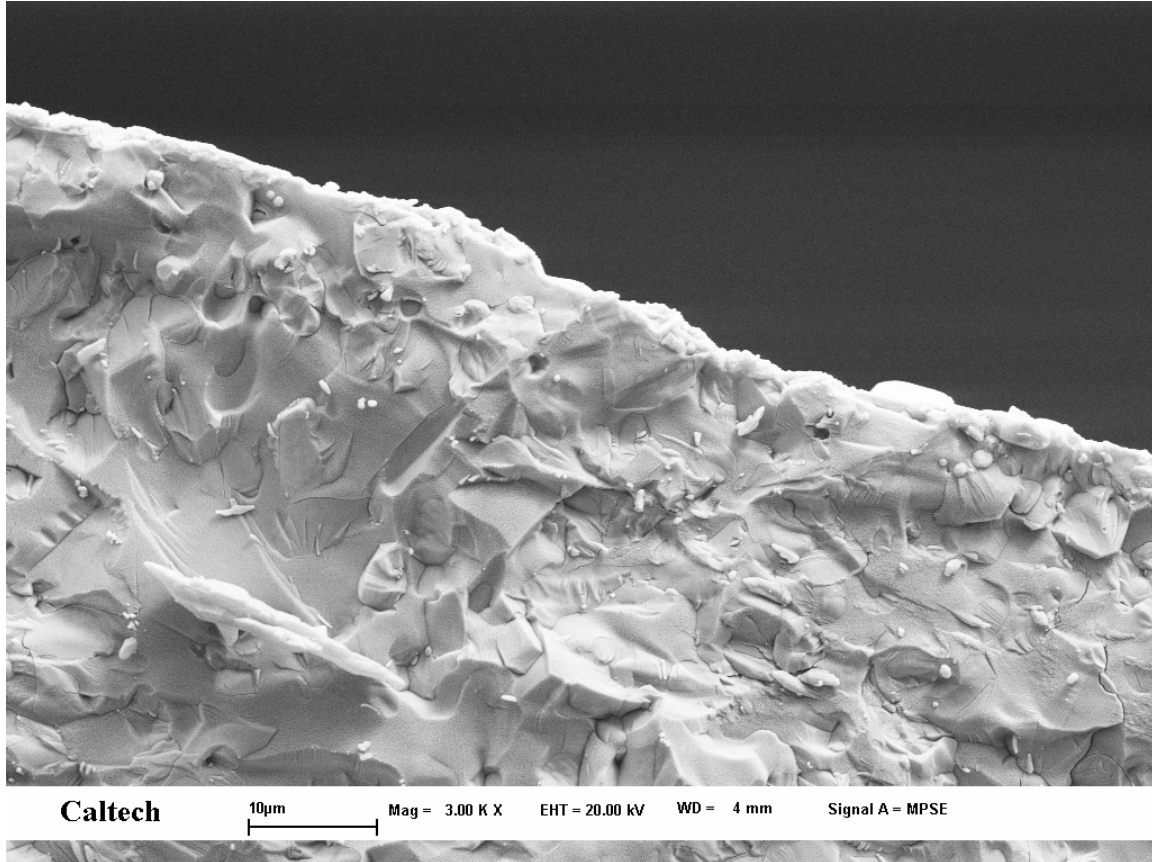


Figure 1. SEM of cross section of glass tube after heat treatment but before leaching.

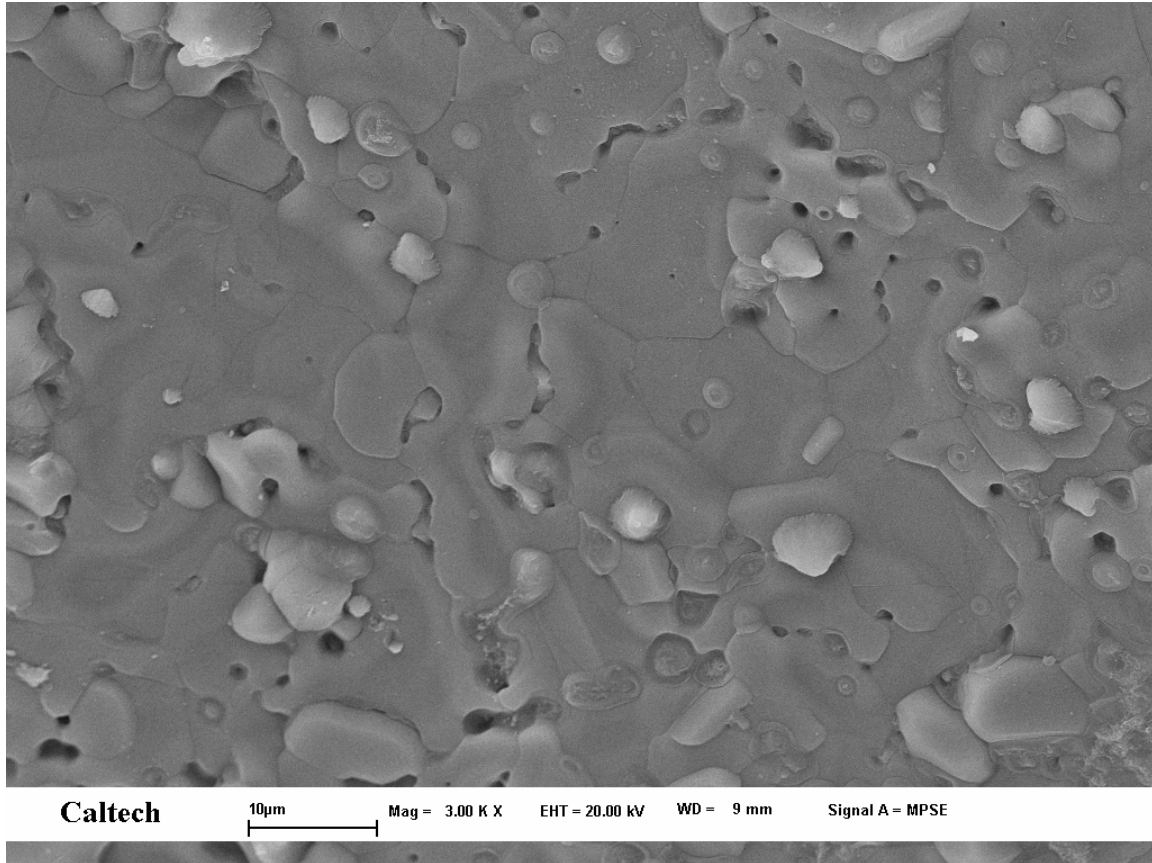


Figure 2. SEM of surface of glass tube after heat treatment but before leaching.

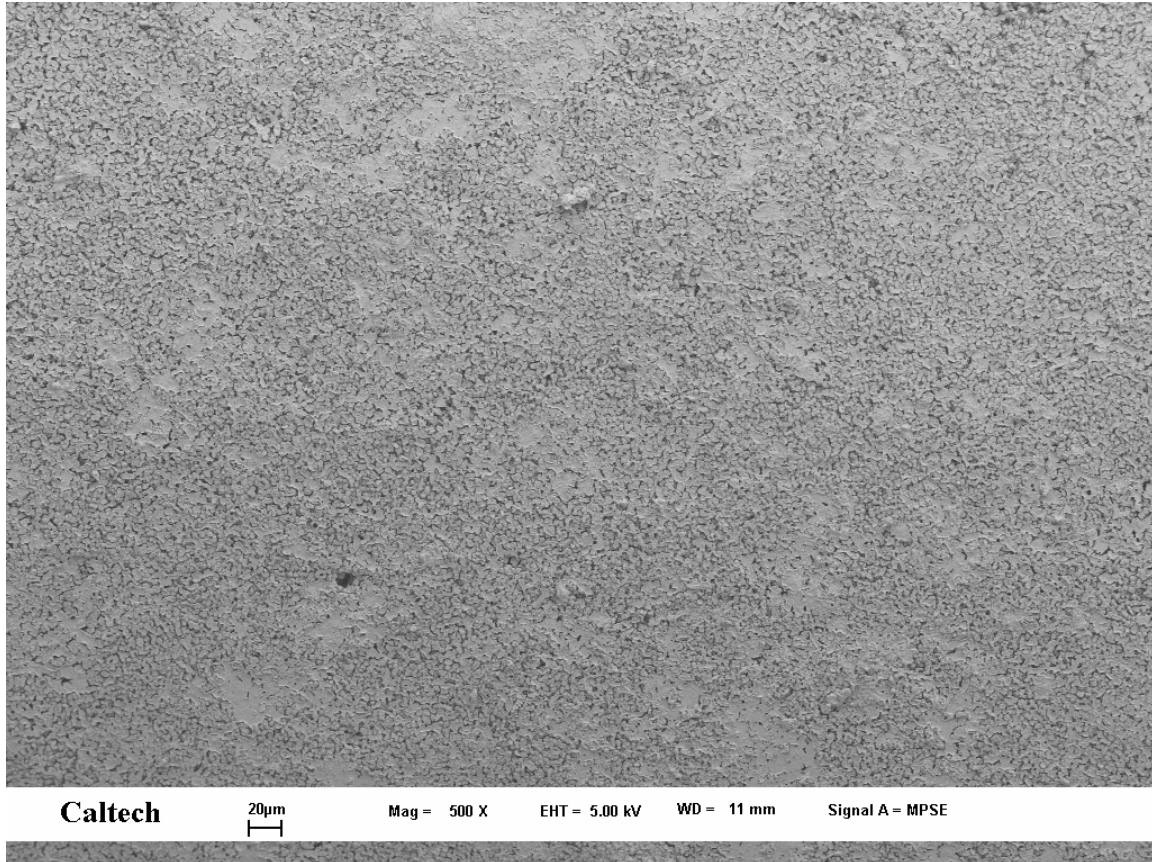


Figure 3. SEM of surface of glass tube after heat treatment and leaching.

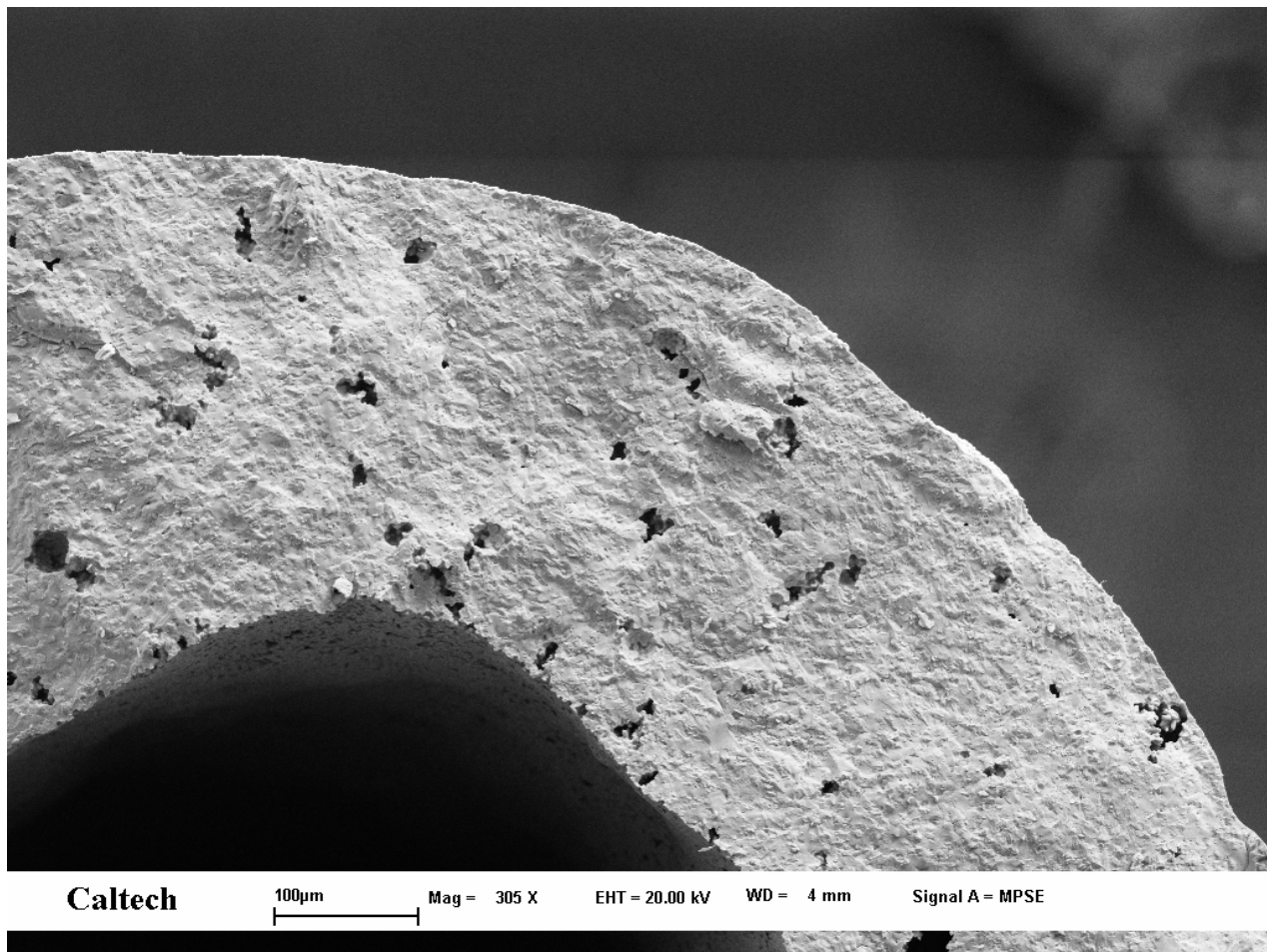


Figure 4. SEM of another glass tube cross section after heat treatment but before leaching.