

# DEVELOPMENT OF POROUS CERAMIC MEMBRANES FOR A SOLAR THERMAL WATER-SPLITTING REACTOR

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The efficiency of hydrogen production by solar thermal water splitting (HSTWS) depends strongly on reactor temperature. The process must be conducted at least at about 2100 °C, in order to be of practical significance. Stabilized zirconia, with a maximum useful temperature of 2300 °C, is a suitable HSTWS reactor construction material. A crucial element in the solar thermal water-splitting reactor is the porous ceramic membrane that enables separation of hydrogen from the hot water splitting reaction products. Zirconia porous membranes are manufactured by powder sintering at about 1800 °C. When such a membrane is exposed in the solar reactor to a higher temperature, it loses its gas permeability due to pore closure by continued sintering. Efforts were made to inhibit the membrane sintering process and to postpone its fast occurrence to higher temperatures, by the use of special stabilized zirconia powders consisting of particles with a rounded shape. The fast sintering of membrane samples made of a homogeneous powder of relatively large spherical particles, prepared by the Sol-Gel method, occurred at some 200 °C above the normal zirconia sintering temperature. The overall picture gathered from our experiments suggests, however, that it will be hardly possible to bridge the temperature gap between the normal sintering temperature of stabilized zirconia and the HSTWS reactor temperature, by the use of stabilized zirconia powders of a particular morphology.

**Keywords:** solar hydrogen production; zirconia membranes; microspherical powder ceramics.

## Introduction

Water vapor can be dissociated by exposure to a high temperature at reduced pressure. In the hydrogen production process by solar thermal water splitting (HSTWS), water vapor is heated by highly concentrated solar radiation and is partially dissociated. Hydrogen is separated from the hot mixture of water dissociation products by gas diffusion. Part of the gas mixture is extracted from the reactor cavity by diffusion through a porous ceramic membrane. It is enriched with hydrogen. The oxygen-enriched gas mixture leaves the reactor cavity bypassing the porous membrane (1).

The thermodynamic efficiency of a HSTWS reactor increases with increasing reactor temperature. The results of an extensive computer simulation study indicate that a temperature of at least 2100 °C must be maintained in the reactor, for the process to be of practical value (2). The inner structural components of the reactor can be manufactured from stabilized zirconia, a material that exhibits chemical, mechanical and thermal stability and fair thermal shock resistance up to 2300 °C. The porous ceramic membrane utilized for hydrogen separation by gas diffusion presents, however, a special problem. Porous ceramic membranes are obtained by sintering powders at a high temperature. Zirconia powders are sintered at 1700–1800 °C. When a porous zirconia membrane is subject to a temperature exceeding its normal sintering temperature, the sintering process continues resulting in loss of gas permeability, due to membrane densification and pore closure (1).

In an effort to develop zirconia porous membranes useful for our application, we tried to inhibit the sintering process and to postpone its fast occurrence to temperatures beyond the working temperature of the HSTWS reactor, by the use of special zirconia powders consisting of particles with a rounded shape. The results of this study are reported below.

## Experimental Procedure and Results

**Composition of Powders for Membrane Sample Preparation.** The fast clogging of a porous zirconia membrane exposed to an elevated temperature is illustrated by the two SEM  $\times$  500-magnification photographs of Figure 1. These photographs were taken after 2 h and 22 h of exposure to 1750 °C, respectively. The membrane sample shown in Figure 1 was made of a CaO-stabilized zirconia powder that was prepared by repeated pelletization, calcining at 1600 °C for 24 h, milling and collection of the relatively coarse particle powder.

Dr. R. Fischer, of the Israel Ceramics and Silicates Institute (ICSI), Haifa, Israel, suggested that the fast sintering of zirconia membranes, made of powders consisting of quasi-spherical or of spherical particles, would be hindered and delayed to higher temperatures. We solicited the collaboration of ICSI in the development of porous membranes characterized by improved stability with respect to pore closure at high temperature.

In order to determine the stabilized zirconia composition suitable for our purpose, ICSI prepared samples of zirconia powder doped with 5.6, 8 and 12% yttria. They were sintered at 1700 °C for 5 h. Subsequently, they were exposed in a solar furnace to 1900 °C for 1.5 h. The ZY-8 and ZY-12 ceramic samples preserved their original shape, whereas the ZY-5.6 sample disintegrated into powder. An XRD analysis of the heat-treated samples showed that the ZY-8 and ZY-12 ceramics were monophase tetragonal and cubic, respectively, while the ZY-5.6 ceramic underwent partial tetragonal-monoclinic phase transition. Obviously, phase transition is the cause of the sample destruction.

The ZY-8 composition was chosen as the basic material for the preparation of stabilized zirconia samples.

We obtained from ICSI two series of stabilized zirconia membranes for the experiment. One series consisted of samples made of spheroidal particle powders. The powders utilized in the preparation of the second series of samples consisted of homogeneous spherical particles obtained by the Sol-Gel method.

**Membranes Made of Spheroidal Particle Powders.** The particle-size range of powders used in the preparation of the first series of membrane samples is listed in Table 1. The samples were sintered at 1850 °C for 1 h. They were then fired at 1700 °C for 33.7 h in an electric furnace. All these samples were cracked after the firing.

The features of the membrane microstructure degradation, following the 1700 °C/33.7-h firing period, are depicted in Figures 2-4.

The SEM × 5000-magnification picture of a membrane particle (Figure 2a) was taken after a 1850 °C/1-h sintering. The particle consists of 1-5- $\mu$ m granules. After the additional firing at 1700 °C/33.7-h (Figure 2b), the big granules grew bigger by diffusion of material from smaller neighboring granules. The granule mean linear size grew more than twofold. Small cracks developed between adjacent granules. At the SEM × 500-magnification level (Figure 3a,b), it is observed that as a result of the prolonged additional firing, clusters of particles are formed by interparticle bridges. The clustering process implies apparently stress generation between neighboring clusters, which leads to initiation of fissures (Figure 3b). The SEM × 50-magnification picture (Figure 4) exhibits mature cracks across the sample.

**Membranes Made of Spherical Particle Powders.** The Sol-Gel process of ceramic powder production eliminates milling and granulation operations. This method enables production of free flowing powders consisting of homogeneous microspheres of a predetermined size. Low sinterability of these powders was expected, in view of their morphology.

In the second series of membrane samples, prepared at ICSI from 8% yttria-stabilized zirconia powders by the Sol-Gel method, the main variable was the diameter of the powder particle. Membrane samples were prepared from microspherical particle powders, the particle diameter varying at the range  $25 \mu\text{m} \leq d \leq 50 \mu\text{m}$ . The samples were sintered for 5 h at 1700-1750 °C. Then they were fired in the solar furnace at higher temperatures.

**Table 1. Spheroidal Particle Powders**

Powder designation	Particle morphology	Particle size ( $\mu\text{m}$ )
FZ1	Spheroidal	35-45 + submicron fines
FZ2	Spheroidal	95-110 (50%) + 15-30 (50%)
FZ3	Spheroidal	22-44 (no fines)
FZ4	Spheroidal	10-20 (no fines)
FZ1'	Spheroidal	As FZ1 - with a fraction at the 15-20 range
JZ1	Spheroidal - with improved sphericity	20-44
JZ3	Spheroidal - with improved sphericity	53-63
JZ2	Spheroidal - with improved sphericity	63-74
JZ2	Spheroidal - with improved sphericity	> 74
JZ4	Spheroidal - with improved sphericity	< 20
A3	Non-spherical	3

Figure 5a is a SEM  $\times 500$ -magnification picture of a sample made of a powder of  $d \leq 25\text{-}\mu\text{m}$  particles sintered at  $1750\text{ }^\circ\text{C}$  for 5 h. After an additional treatment at  $1900\text{ }^\circ\text{C}/1.5\text{ h} + 1980\text{ }^\circ\text{C}/1.5\text{ h}$ , the porous structure of the sample was completely destroyed (Figure 5b). By contrast, another sample made from a  $d \geq 50\text{-}\mu\text{m}$  powder emerged from the same heat treatment sequence with almost unchanged open porosity ( $OP \approx 35\%$ ) (Figure 5c). A similar heat treatment "surviving" sample made of a  $d = 35\text{-}\mu\text{m}$  powder was exposed to an additional  $1750\text{ }^\circ\text{C}/33.7\text{-h}$  firing in an electric furnace. It still preserved its porous structure, but some of the microspherical particles were split (Figure 6).

### Conclusions

Our attempts to develop porous membranes from stabilized zirconia that undergo fast sintering at temperatures much higher than the normal zirconia sintering temperature met only with partial success. With membrane samples made of a homogeneous powder of relatively large spherical particles, prepared by the Sol-Gel method, we were able to demonstrate considerable retardation ( $\sim 200\text{ }^\circ\text{C}$ ) of membrane blocking up by sintering.

The overall picture gathered from our experience suggests, however, that it will be hardly possible to bridge the ca.  $500\text{ }^\circ\text{C}$  gap between the normal sintering temperature of stabilized zirconia and the reactor operating temperature by powder doping or by the use of powders of special particle morphology.

Besides metal oxides, there are other refractory materials that melt and sinter at extremely high temperatures, as seen in Table 2. We were reluctant to consider the utilization of membranes made from these materials, because we foresaw that they would undergo chemical attack in the presence of the water splitting reaction products. When this issue was brought up during a discussion with Dr. P. Bardham, Head of the Cellular Ceramics Division at Corning Corporation, he observed that some of the above-mentioned materials, when exposed to HSTWS working conditions, might develop a thin protective layer that would prevent their disintegration by chemical attack.

Efforts will be made to obtain samples of such materials and test them at HSTWS reactor working conditions.

Table 2. Some High Melting Point Ceramics

Carbides	Melting point ( $^\circ\text{C}$ )	Borides	Melting point ( $^\circ\text{C}$ )	Nitrides	Melting point ( $^\circ\text{C}$ )
TiC	3160	TiB	2980	TiN	2930
ZrC	3030	ZrB	3040	ZrN	2980
HfC	3890	HfB	3100	HfN	3310

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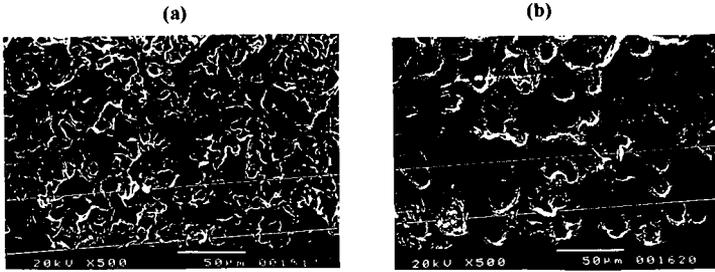


Figure 1. ZY-8-stabilized zirconia porous membrane from (-100/+325) powder. (a) After 1750 °C/2 h. (b) After 1750 °C/22 h.

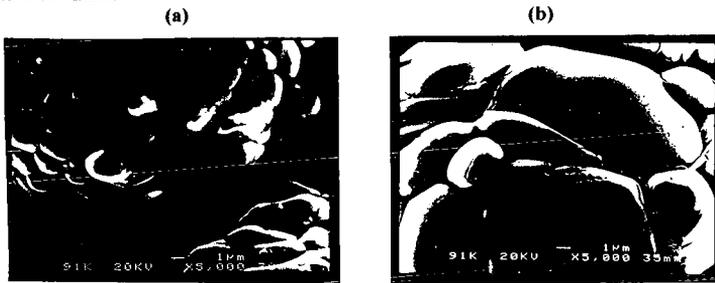


Figure 2. FZ1 + A3 membrane – SEM  $\times$  5000. (a) After 1850 °C/1 h. (b) After 1850 °C/1 h + 1700 °C/33.7 h.

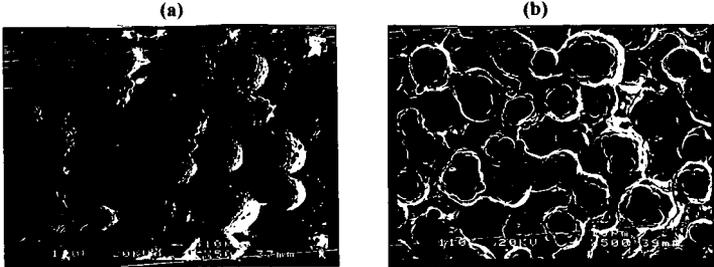


Figure 3. FZ1 + A3 membrane – SEM  $\times$  500. (a) After 1850 °C/1 h. (b) After 1850 °C/1 h + 1700 °C/33.7 h.

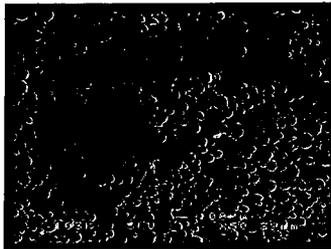


Figure 4. FZ2 + A3 membrane – SEM  $\times$  50. After 1850 °C/1 h + 1700 °C/33.7 h.

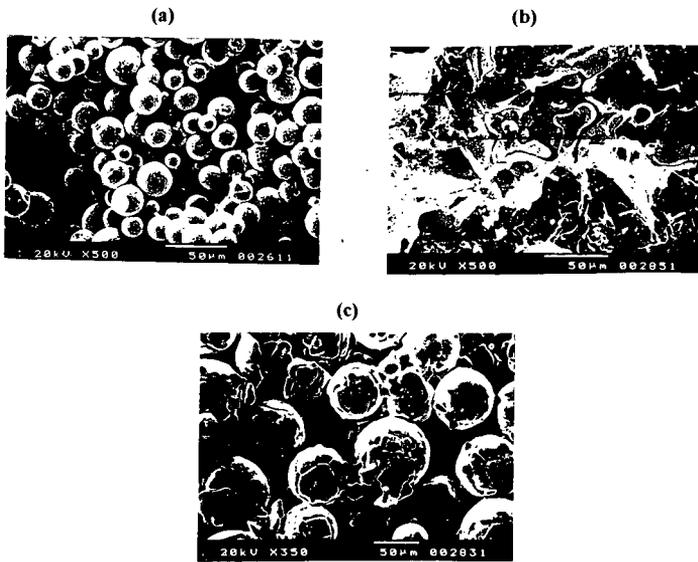


Figure 5. Membrane from Sol-Gel powder. (a)  $d \leq 25 \mu\text{m}$  particles,  $1750 \text{ }^\circ\text{C}/5 \text{ h}$ . (b)  $d \leq 25 \mu\text{m}$ ,  $1750 \text{ }^\circ\text{C}/5 \text{ h} + 1900 \text{ }^\circ\text{C}/1.5 \text{ h} + 1980 \text{ }^\circ\text{C}/1.5 \text{ h}$ . (c)  $d \geq 50 \mu\text{m}$ ,  $1750 \text{ }^\circ\text{C}/5 \text{ h} + 1900 \text{ }^\circ\text{C}/1.5 \text{ h} + 1980 \text{ }^\circ\text{C}/1.5 \text{ h}$ .

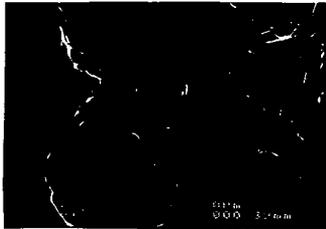


Figure 6. Membrane from Sol-Gel powder –  $d = 35 \mu\text{m}$ ,  $1750 \text{ }^\circ\text{C}/5 \text{ h} + 1900 \text{ }^\circ\text{C}/1.5 \text{ h} + 1980 \text{ }^\circ\text{C}/1.5 \text{ h} + 1750 \text{ }^\circ\text{C}/33.7 \text{ h}$ .