Development of Silica Aerogel with Any Density


Abstract—New production methods of silica aerogel with high and low refractive indices have been developed. A very slow shrinkage of alcogel at room temperature has made possible producing aerogel with high refractive indices of up to 1.265 without cracks. Even higher refractive indices than 1.08, the transmission length of the aerogel obtained from this technique has been measured to be about 10 to 20 mm at 400 nm wavelength. A mold made of alcogel which endures shrinkage in the supercritical drying process has provided aerogel with the extremely low density of 0.009 g/cm$^3$, which corresponds to the refractive index of 1.002. We have succeeded producing aerogel with a wide range of densities.

I. INTRODUCTION

Silica aerogel has been widely used as Cherenkov radiators in high energy experiments. The method for producing aerogel with refractive indices of 1.01 to 1.07 was developed in the previous studies [1], [2]. To obtain more transparent aerogel with the above range of refractive indices, a new solvent has been introduced in the sol-gel step [3], [4].

However, it was difficult to produce aerogel with higher and lower refractive indices and a certain amount of volume for the following reasons:

1. for higher refractive index
   Compared to methylalkoxide oligomer, solvent is small in amount. The sol-gel process does not appear to progress.

2. for lower refractive index
   In the supercritical drying process, aerogel with extremely low target refractive indices heavily shrinks by nature. The resultant aerogel had higher refractive indices than desired.

It is important to mention here that there is the following relationship between the refractive index $n$ and the density $\rho$ of silica aerogel: $n = 1 + \alpha \rho$, where $\alpha \sim 0.25$ cm$^3$/g is the constant. Since the transparency of aerogel with extremely low refractive indices is too low for the refractive index to be measured, not $n$ but $\rho$ is useful for the discussion as to aerogel with low refractive indices.

It is known that aerogel with higher refractive indices than 1.07 is obtained by annealing aerogel with temperature higher than 900°C. The resultant aerogel have the uneven refractive indices and the low transparencies. In contrast, aerogel with refractive indices of 1.01 to 1.005 has produced by using a glass mold and a thin glass plate put on the alcogel in the supercritical drying process. The electrical force of attraction between alcogel and glass would decrease shrinkage. The aerogels with refractive index of 1.007 were used in the KEK proton synchrotron E248 experiment [5] and the SPring-8 LEPS experiment [6].

These arguments point to a need for controlling shrinkage of alcogel in order to develop aerogel with higher and extremely low refractive indices. The present paper will report on the first result from our attempts to control the refractive index or the density of aerogel.

II. PRODUCTION METHODS

A. Pinhole Drying Method

In general, to control the refractive index of aerogel, the molar ratio of each solution is adjusted before being mixed. A relative decrease in solvent produces higher refractive index.

In the pinhole drying method, which is our new technique for producing aerogel with higher refractive index, the mixing ratio for higher is not employed. An alcogel with target refractive index of ~1.05 where aerogel has lower refractive indices than desired is prepared. The resultant aerogel had higher refractive indices than desired.

Manuscript received November 11, 2005.

M. Tabata, T. Fukushima and A. Kuratani are with the Graduate School of Science and Technology, Chiba University, Chiba, 263-8522 Japan (e-mail: makoto@hepburn.s.chiba-u.ac.jp, tomokazu@hepburn.s.chiba-u.ac.jp and kuratani@hepburn.s.chiba-u.ac.jp).

I. Adachi and S. Nishida are with IPNS, the High Energy Accelerator Research Organization (KEK), Tsukuba, 305-0801 Japan (e-mail: ichiro.adachi@kek.jp and shohei.nishida@kek.jp).

H. Kawai and H. Nakayama are with the Faculty of Science, Chiba University, Chiba, 263-8522 Japan (e-mail: kawai@hepburn.s.chiba-u.ac.jp and hiron@office.chiba-u.ac.jp).

H. Kishimoto and H. Yokogawa are with the New Business Planning Office, the Matsushita Electric Works, Ltd., Osaka, 571-8686 Japan (e-mail: klishi@rda.mew.co.jp and yokogawa@mewa.mew.co.jp).

T. Noguchi is with the Faculty of Science, Ibaraki University, Mito, 310-8512 Japan (e-mail: tngc@mx.ibaraki.ac.jp).

K. Okudaira and H. Yano are with ISAS, the Japan Aerospace Exploration Agency (JAXA), Sagamihara, 229-8510 Japan (e-mail: okudaira@planeta.sci.isas.jaxa.jp and yano.hajime@jaxa.jp).

Y. Tajima and H. Yoshida are with the Faculty of Science, Yamagata University, Yamagata, 990-8560 Japan (e-mail: tajima@sci.kj.yamagata-u.ac.jp and yoshida@ksquark.kj.yamagata-u.ac.jp).

0-7803-9221-3/05/$20.00 ©2005 IEEE
the alcogel with desired density produces the aerogel with any refractive index which is higher than initial. After the pinhole drying, the alcogel is sunk in ethyl alcohol and dealt with by the usual means. The shrunk alcogel does not expand again.

**B. Frame Structure Method**

A monolithic aerogel block consisted of multiple layers with different refractive indices has been developed as the radiator of a ring imaging Cherenkov (RICH) counter [3], and it is not broken away after the supercritical drying process. The technique combined with the method of using a glass mold and a thin glass plate can be applied to development of aerogel with extremely low density. An alcogel which does not shrink in the supercritical drying process due to having somewhat higher density (refractive index $n > 1.01$) is formed in a glass mold, and then another alcogel mixed for extremely low density by using ethyl alcohol as solvent is put on the first alcogel. A chemical force of attraction on the boundary between alcogels should almost completely prevent the upper alcogel from horizontal shrinkage.

Moreover, in order to avoid vertical shrinkage, all or except the top sides of the upper alcogel is surrounded by an alcogel with higher density: a frame made of alcogel is used as a mold for aerogel with extremely low density (Fig. 3).

**III. RESULTS**

**A. High Refractive Index**

Aerogels in good condition has produced by using glass cases and stainless-steel sand strainers. The application of the pinhole drying method to aerogels with the initial refractive indices of 1.024 to 1.060 has produced aerogels with refractive indices of 1.034 to 1.265. The measurement of the refractive index was done using the Fraunhofer method with a 405 nm laser. Fig. 4 indicates that shrunk aerogel almost maintain its initial transparency. It is our expectation that aerogel produced in the pinhole drying method should have higher transparency than that produced directly.

Fig. 4. Transmission length at 400 nm wave length as a function of refractive index for pinhole drying method samples. "Reference" is not used the pinhole method. The aerogels produced at the same time as references with the refractive index of ~1.05 obtain refractive indices of 1.10 to 1.265 in the method.

Fig. 5 shows a high refractive index sample produced in the pinhole drying method. Practically, there are some aerogels with crack, but the sample has not any crack.
As can be seen in Fig. 6, the densities of an aerogel broken to pieces have been measured. There is no measurable difference in the density of each part.

**B. Low Refractive Index**

In the samples more than 20, the frame structure method has been useful for avoiding shrinkage of alcogel. Two samples are shown in Fig. 7, 8.

![Fig. 7. Photograph of an aerogel consisted of multiple layers with different refractive indices. This is low refractive index sample. Density: 0.0123±0.0011 g/cm³ (upper aerogel)](image)

Through these aerogel samples with low density, we can easily read a newspaper.

**IV. CONCLUSION**

The production methods of aerogel with any densities between liquid and gas materials have been demonstrated. A Cherenkov counter used this aerogel with the refractive index of around 1.20 may be applied as a new gamma detector of positron emission tomography (PET) [7]. An attempt to introduce heavy metal such as Pb into aerogel without decreasing the transparency is under way.

The aerogel with extremely low density will be employed as a cosmic dust collector [8]. To catch cosmic dusts softly, aerogel with as low density as possible is required. An aerogel with the density of ~0.005g/cm³ would be produced soon.

**ACKNOWLEDGMENT**

We thank Y. Tanaka at Chiba University for cooperating in the measurements of density.

**REFERENCES**


