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Measuring the Pore Sizes of Sol-Gels Using Argon Effusion Techniques

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Abstract

The rate of effusion of argon through a sol-gel scaffold will be measured to determine the size of the pores. The effusion rate will then be used to correlate initial pore size to any pore shrinkage that occurs. We will attempt to control the initial pore size by using various-sized paraffin beads as templates throughout the organically modified tetramethoxysilane (TMOS) gel scaffold. Polyethylene glycol (PEG) will also be used to prop open the pore openings and keep them from closing during the drying process.

Introduction

Most conventional glasses that are formed are of a uniform, homogeneous type. One characteristic of sol-gels allows the glasses to be formed by the mold. The mixtures that form the sol-gels are optically transparent porous glasses. They can be modified by incorporating an organic phase into the sol-gel forming an inorganic-organic hybrid. The ability to incorporate any organic phase into the sol-gel allows for specialization of the sol-gel. The sol-gel process enables the preparation of numerous types of new inorganic-organic materials, which are impossible or are extremely difficult to synthesize by any other process. "Sol-gel processes may be divided into two types depending on the nature of the precursors: inorganic (chlorides, nitrates, sulfides, etc.) and alkoxide-based precursors." The formation of an inorganic-organic hybrid occurs by either pre-doping or post doping. In pre-doping, the organic part becomes a part of the sol-gel structure. In post doping, both the organic and inorganic phases exist physically and are chemically identifiable. These hybrids can be formed by dissolution of an organic in the sol-gel, impregnation of an organic, reacting an inorganic that already has a chemically bonded organic group such as $CH_3Si(OCH_3)_3$, or reactions occur in the liquid solution between the two components to form chemical bonds in the hybrid gel. The new sol-gels that are formed are used in the study of "porous

membranes, sensors, thermal insulation, dense protective films and passive optical films, active optical films, and bulk optics."

Theory

An effusion device was created from a piece of stainless steel pipe to be used to measure the pore size of a sol-gel. First, the volume flow (F) of the argon exiting the effusion apparatus was determined by timing the displacement of 2.0×10^{-3} m3 of water.

$$E = FN \qquad (1)$$

The particle flow (E) can be found by multiplying the volume flow by the particle density (N). The particle density can be found from the ideal gas law as shown below.

$$N = \frac{pN}{RT} \qquad (2)$$

Where p is the ambient pressure, N is Avogadro's number, R is the universal gas constant, and T is temperature.

$$E = \frac{pAN}{(2\pi MRT)^2} \qquad (3)$$

When a gas at a certain pressure and temperature is separated by a vacuum by a small hole, the rate of escape of its molecules is equal to the rate at which they strike the area of the hole. By substituting equation 2 into equation 1 E can be found. Then substituting E into equation 3 and rearranging, equation 4 is obtained. The cross sectional area is determined by:

$$A = \frac{E(2\pi MRT)^2}{pN} \qquad (4)$$

M is the molar weight of argon. Assuming the pore cross-section to be a circle the radius can be calculated.

Procedure

To make the sol-gel the following recipe was used. It should be noted that the original recipe had the amounts of water, methanol, HCl, and TMOS in units of volume (_L). These amounts were converted to grams to facilitate the transfer of the reagents. The silica solution was made by mixing approximately 3 grams of methanol with 8 grams of TMOS. The catalyst solution, 1.5 grams of H2O and 1 drop of HCl, was added dropwise at a rate of 1 drop/5 seconds to the silica solution while stirring. After five days of stirring the sol-gel was cast into a large test tube using a micro-pipet. The test tube was sealed with parafilm and allowed to sit until the solid sol-gel was formed.

The paraffin beads were prepared by first melting Gulf Wax® paraffin in a beaker in a hot water bath. A solution of 5 grams of polyvinyl alcohol (PVA) with 100 mL of H2O was made. Heat was applied to the PVA solution while stirring until the solution reached a temperature of 65∞C. Approximately 25 mL of melted wax was slowly poured into the PVA solution while stirring vigorously. Ice water was poured into the wax/PVA mixture to solidify the paraffin beads. The beads were allowed to air dry one week and then separated using various size sieves ranging from 160 mm to 250 mm. After separation, the beads were ready to be added to the sol-gels.

When the beads were incorporated into the sol-gel, the same sol-gel recipe from above was used. The only difference was that the beads were added to the silica solution before the catalyst was added.

The recipe for the 400 mw PEG used the same ingredients as the above sol-gels, except the PEG (1 gram) was added to the silica solution and then the catalyst. After about two days, half of the PEG doped sol-gel was cast in a test tube and the other half was cast into the stainless steel effusion device. Both tubes were covered with parafilm and allowed to dry via evaporation.

Results

The first batches of sol-gels were blank sol-gels, meaning no dopants were added. The blanks were used as standards to make sure that the effusion system worked effectively. The usual shrinkage of the sol-gel, due to the evaporation of the solvent, was

experienced. The course taken to minimize the shrinkage of the sol-gel was to have the sol-gel form around paraffin wax beads. A blank sol-gel was used to determine the pore sizes by using the argon effusion techniques.

When the beads were added to the sol-gel mixture, the beads would stay in the solution for awhile. After mixing for about a day the beads would start to float to the top of the mixture and would not stay in solution, thus not allowing the sol-gel matrix to form around the beads and control the pore size (Figure 1). In an attempt to correct this occurrence, 0.5 mL of sodium heptadecyl sulfate, a surfactant, were added in an attempt to keep the beads in the solution so the matrix could form around them.

With the surfactant in solution, the paraffin beads were added to the solution. For the first day, the surfactant worked and the beads stayed in solution, but after a day of stirring, the beads once again started to float to the top of the mixture. Upon the first examination, it appeared that this approach did work, but when a piece of the sol-gel was examined under the SEM, no beads were found to be present within the sol-gel scaffold (Figure 2). The cause of the beads floating in the mixture was because the beads are less dense than the mixture. With this discovery, the decision was made to abandon the paraffin beads and begin using the PEG to keep the pores open.

Using PEG as a dopant to prop the sol-gel pores open is a technique proven to prevent the shrinkage of the sol-gel. The sol-gel did form to the shape of the test tube so the sol-gel was useable in the argon effusion apparatus. One problem encountered was that the sol-gel was not dry all of the way and cracking of the scaffold was observed. The sol-gel did not come apart completely so it was still useable in the effusion apparatus. See Table 1 for results. Possible error in the readings from the flow meter were due to the cracks in the sol-gel, and thus the argon passed through faster than it would have if there had been no cracks. Also since the gel did not completely seal off the end of the apparatus the argon was unhindered in passing through the openings.

Conclusion

More sol-gels are in the process of being made so that the research can continue to collect data and work towards more reliable

conclusions. The applications of the sol-gel will be determined by its final properties. For optical purposes, the gel will need to be completely transparent with the minimalist amount of flaws in the gel so that the source can pass through it. It will also be helpful if the gel does not have any cracks in it. If the gel is going to be used for filtration purposes then it does not matter if the gel is transparent because the gel will be powdered and put into a column for further use.

Acknowledgements

Figure 1   Figure 2

Sol-Gel	400 mw PEG
Velocity of Ar	7.487 m/s
Rate of Effusion	2.881×10^{18} s^{-1}
Cross Sectional Area	2.386×10^{-6} m^2
Radius	8.716×10^{-4} m

Table 1 is the results of the PEG doped sol-gel

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