State-of-the-art of Metamaterials: Aerogel's characterization, realization and applications

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Abstract–Metamaterials is a large family of artificial composite structures or composite materials that have some specific extraordinary properties which natural materials do not possess. Aerogel is one kind of them. Following a description of the properties and preparation technology of aerogel, this paper explores recent literature on the use of aerogel in the research areas of heat, acoustics, microelectronics, etc. This contribution is meant to provide an overview of their applications in architecture and space, etc.

Keywords: Metamaterials, Aerogel

Introduction

Aerogel is a new lightweight nano porous amorphous solid material.[1]Due to the unique nano porous structure, its properties are obviously different from macroscopic glassy materials.The unique properties of aerogel include: 'high surface area(>1000m^2/g), low refractive index(<1.1), low conductivity(<1.7), low conductivity(˜0.017W/m*K), low propagation speed(<100m/s) and low density(<100kg/m^3)'[2] Especially the low density, aerogel is a material that is 99.8% air, thus it's the least dense solid in the world. With the deepening of research, its potential application value is constantly being reflected. They are mainly focused on the fields of heat, adsorption, catalysis and electronics.[3]

Discovery

In 1931, Steven.S.Kistler from College of the Pacific, United States, expected to prove that a solid 'gel' with a continuous network structure of the same size has the same shape as the wet gel, and it would be direct and effective by proving that it is possible to replace the liquid in the gel with gas without changing the solid structure. Based on the speculation that the solid composition of the gel was porous, and when the liquid evaporates, there was a larger surface tension at the liquid-gas interface, which leaded to the collapse of the channel, 'Kistle prepared hydrogels using sodium silicate as silicon source and hydrochloric acid as catalyst, and then prepared silica aerogel for the first time through solvent replacement and ethanol supercritical drying.'[4]

Since then, aerogel of a variety of materials, such as aluminium oxide and aluminium oxide, has been made.

Preparation

The aerogels can be divided into three categories– inorganic aerogels (such as SiO_2 aerogels and Al_2O_3 aerogels), organic aerogels (such as resorcinol formaldehyde aerogels and melamine formaldehyde aerogels) and carbon aerogels obtained from the carbonization of organic aerogels.

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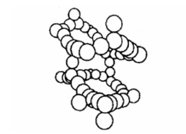

Figure 1. The stucture of SiO_2 aerogel[5]

'The preparation of aerogel consists of two processes: sol gel process and drying process.'[6]

For inorganic aerogels, silicon aerogel is the most aerogel studied at present. In sol-gel process, three dimensional network structure silicon aerogel was obtained by hydrolysis and condensation of silicon source material. Its reaction principle is

$$Si(OR)_4 + 4H_2O \quad Si(OH)_4 + 4HOR \qquad \text{(hydrolysis)}$$
$$nSi(OH)_4 \quad (SiO_2)n + 2nH_2O \qquad \text{(polycondensation)[7]}$$

'By adjusting the acidity and alkalinity of the reaction solution, the gel structure can be obtained by controlling the relative rate of hydrolysis reaction and condensation reaction in hydrolyzation-condensation process. Under strong alkaline or high temperature conditions, the solubility of SiO2 increases, the formation of colloidal aggregates formed by smooth surface microspheres under the action of surface tension.'[8]

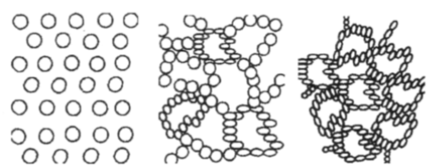

Figure 2. Formation schematic diagram of silica aerogel [9]

For organic aerogels, resorcinol formaldehyde is the most aerogel studied at present. 'In 1989, Pekala, from Lawfnce Livemore National Laboratory of the United States, prepared the organic aerogel successfully for the first time using resorcin and formaldehyde as raw materials, and then carbonized in an inert atmosphere to prepare carbon aerogel.'[10] 'The first step is addition reaction– resorcinol and formaldehyde form single/multiple hydroxymethyl resorcinol under the catalysis of alkali(such as sodium carbonate). Then, the condensation reaction conducts which occurs between the hydroxymethyl(-CH_2OH) of the intermediate single/poly hydroxymethyl resorcinol and the position that is not replaced on the benzene ring, and the colloidal particles formed by methylene bonds

(CH_2 -) and methylene ether bonds (CH_2OCH2 -) are formed respectively.'[11]

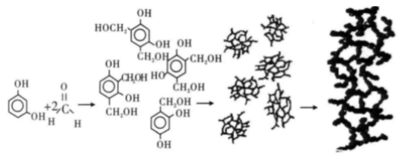

Figure 3. Formation schematic diagram of RF aerogel [11]

In terms of the drying process, supercritical drying is one classical method and the most effective method to obtain complete structure aerogel. 'Its principle is through high temperature and high pressure to make the drying medium reach supercritical state, eliminate the gas liquid interface. Meanwhile, this method effectively avoids the occurrence of surface tension, and maintains the good performance of the gel. The most commonly used media are ethanol alcohol and carbon dioxide.'[1]

Drying media	Boiling point℃	Critical temperature ℃	Critical pressure MPa
Carbon dioxide.	-78.5	31.1	7.29
Ammonia gas	-33.4	135.2	11.33
Methyl alcohol	64.6	239.4	7.99
Ethanol alcohol	78.3	243	6.3
Benzene	80.1	288.9	4.83
N-propyl alcohol	82.2	235.1	4.7
Isopropyl alcohol	97.2	263.5	5.1
Water	100	374.1	21.76

Figure 4. Critical parameters for some drying mediums [12]

However, because of its expensive equipment and difficult process control, and it has become the bottleneck of industrial production.Therefore, at present, the main research direction of non-supercritical drying technology is atmospheric drying and freeze drying.

The principle of atmospheric drying–assuming that the pores of the gel are cylindrical pores, according to Laplace's equation , the additional pressure of liquid meniscus in capillary pores can be expressed as follows:

$$\rho=-2\gamma\cos\vartheta/r_m \quad [13]$$

Where γ is the gas-liquid interfacial energy, ϑ is the contact angle, r_m is the pore radius. The additional pressure P acts on the liquid, thus, the compression pressure of the liquid causes the gel network to contract. According to formula, if increasing the capillary radius, or increasing the contact angle and decreasing the interfacial energy of solvent can reduce the additional pressure and reduce the shrinkage of aerogels.[6]

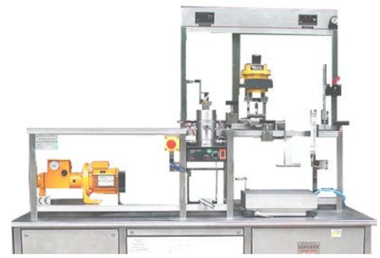

Figure 5. Diagram of supercritical drying equipment

With respect to freeze drying, by lowering the temperature, the gel is frozen, and then the solvent is sublimated, so that the surface tension of the gas-liquid surface disappears, so as to achieve the purpose of drying the aerogels.

'Comparing to the supercritical drying, both freeze drying and atmospheric drying have the advantages of simple operation and low cost, while low success rate, long dry time, easy cracking are their common defects.'[5]

Applications

Many unique properties, such as high porosity, low density, low refractive index and low thermal conductivity, make aerogels widely used in many fields or potential applications.

(1) Thermal insulation material

'At room temperature, the thermal conductivity of SiO_2 aerogels can reach 0.013˜0.016W/(M*K).(the thermal conductivity of static air is 0.024W /(M*K). Even at a temperature of 800, its thermal conductivity is only 0.043W/(M*K).' [14]It is the best solid material with the best thermal insulation. Specific applications cover the area of scientific research, industry, national defense and daily life, especially the aviation, navigation, construction and other thermal insulation places.

(2) Hydrogen storage material

'The new nano porous carbon aerogels have rich nanoscale pores (1 ˜ 100nm), high porosity (> 80%) and large specific surface area (400 ˜ 3200m^2 / g)'[15], thus it is a potential hydrogen storage material, in the case that hydrogen has the highest calorific value except nuclear fuel, and it is the cleanest fuel to burn.

(3) Environmental protection

The high porosity and large surface area of SiO_2 aerogels make it have amazing adsorption capacity. It is found that the removal rate of dyes in dye wastewater by amino modified SiO_2 aerogels is 90% ˜ 100%, so the amino modified nano SiO_2 aerogel is an effective material to purify wastewater containing dyestuff .[16]

Prospects and prospects

After the invention of aerogels in the 1930s, due to the high preparation cost and defects in the preparation process, it has not received much attention from the outside world. Even at present, how to further improve the process, shorten the preparation time, and improve the production rate is the main bottleneck that hinders the expansion and application of aerogel. On the other hand, aerogels are being used in more and more fields due to their superior heat insulation, catalysis, adsorption, insulation and other properties.Therefore, with the continuous improvement of the preparation process, the supermaterials represented by aerogels will be more widely used in more fields and create more social and economic value.

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