Silicon Dioxide [AEROGEL]{SiO2}

By Avni Bhardwaj
SVKMI's NMIMS
School of Technology, Management and Engineering
INDORE

ABSTRACT

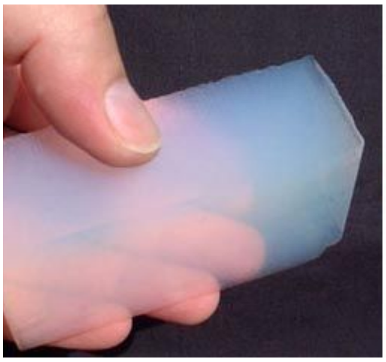
Silica aerogels are popular in terms of production volume and real-world applications. Although the current market growth rate is driven exclusively by thermal insulation, aerogels may also be attractive for acoustic applications with the potential in aiding sound absorption/insulation. This paper is a summary of the acoustics-related studies of silica aerogel-based products. It introduces silica aerogels, and some acoustic characterisation methods, and systematically reviews the available data on sound absorption/insulation of silica aerogels, polymer-silica aerogel composites, non-woven-silica aerogel blankets, and aerogel renders/glazing. The work identifies areas where further research is required, including experimental and theoretical work on the physics of sound absorption in mesoporous materials, and more systematic and standardised evaluations of the acoustic properties of aerogel and aerogel-composites.

In recent years, metal-organic frameworks (MOFs) have attracted incredible chemical and material research interests because of their prominent properties and charming structures. The reliable production of a wide variety of MOF materials and MOF derivatives, such as MOF-metal nanoparticles composites and MOF-polymers hybrids, offers many possibilities to develop MOF-based applied materials. Although MOFs have many unique features, including abundant pore structures and multiple functional ligands, their applied performance is limited by intrinsic fragility and powdered crystalline state, as well as unsatisfied stability and processability. By this, MOF-based hydrogels and aerogels have achieved unparalleled results, outperforming MOF materials in many aspects. This review presents current developments in MOF-based hydrogels and aerogels with an emphasis on the specific categories and the synergistic effects of MOF-derived aerogels between MOFs and additional materials. Particular emphasis is placed on discussing the advantages of MOF-based hydrogels and aerogels in applications such as sensors, batteries, supercapacitors, adsorbents, catalysts etc. MOF-based hydrogels and aerogels can provide valuable guidance for the investigation of MOFs towards practical applications with processability, stability, and easy handling. Specifically, we will summarise the recent progress of pure MOF hydrogels, MOF@biology derived organic macromolecules hydrogels, MOF@biocompatible hydrogels, MOF@ graphene hydrogels, pure MOF aerogels, MOF@silica aerogel composites, MOF@ graphene aerogel composites, MOF@cellulose aerogel composites, and aerogel composites containing MOFs-derived materials.

Eco-friendly electromagnetic wave-absorbing materials with excellent thermal infrared stealth properties, heat-insulating ability and compression resistance are highly attractive in practical applications. Meeting the aforesaid requirements simultaneously is a formidable challenge. Herein, ultra-light carbon aerogels were fabricated via fresh shaddock peel by facile freeze-drying method and calcination process, forming porous network architecture. With the heating platform temperature of 70 °C, the upper surface temperatures of the as-prepared carbon aerogel present a slow upward trend. The colour of the sample surface in thermal infrared images is similar to that of the surroundings. With the maximum compressive stress of 2.435 kPa, the carbon aerogels can provide favourable endurance.

INTRODUCTION

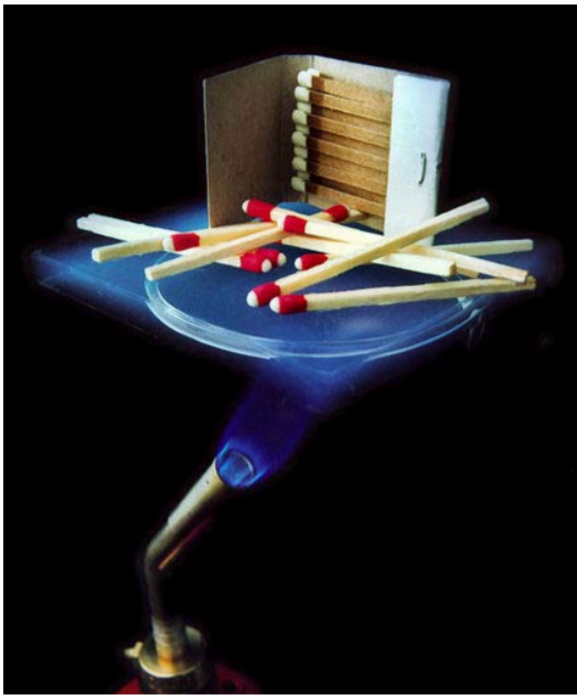
Aerogels, also termed as the world's lightest solid yet at the same time proven to be as hard as steel is a special type of solid material with nanometre-scale pores<1/3000th the width of the human hair. the porosity of an aerogel ranges from 90% and goes until 99.9%. the liquid part of the pores is exchanged by gas without compromising on its shape.



They are essentially 'puffed-up sand', often termed as 'frozen smoke.Their thermal conductivity is the lowest of any solids, having good transparency,lightweight, low density, heat resistance, low refractive index & high specific surface area

This acoustic property of aerogels makes them effective insulators against noise and heat, making them a perfect opportunity for their application in buildings.

It is 99.8% Air . It Provides 39 times more insulation than the best fiberglass insulation and 1,000 times less dense than glass.



Aerogels were first created by Steven Kistler in 1931, as a result of a bet with Charles Learned over who could replace the liquid inside a jam (jelly) jar with gas without causing shrinkage. The first results were silica gels. Aerogel can be made of many different materials; Kistler's work involved aerogels based on silica, alumina, chromia, and tin oxide. Carbon aerogels were first developed in the early 1990s.

Due to their many excellent properties, aerogels attract much interest in various applications, ranging from construction to medicine. Over the last decades, their potential was practically exploited only in non-medical fields of use, although many aerogel materials, either organic, inorganic or hybrid, were proven biocompatible. Some aerogel compositions have been patented at the verge of the millennium, but the clinical use of aerogels remains very limited. This review intends to shed some more light in regard to their potential in biomedical applications as can be deduced from the more recent progressive research of their capabilities in regard to different compositions. The review covers many recent studies, but includes older research that significantly affected the development of aerogel-based materials over the years, as well. After a short introduction, covering the common aerogel properties and their possible classification options, the review is structured based on their different possible biomedical applications. Finally, it focuses on the potential of aerogels in regenerative medicine.

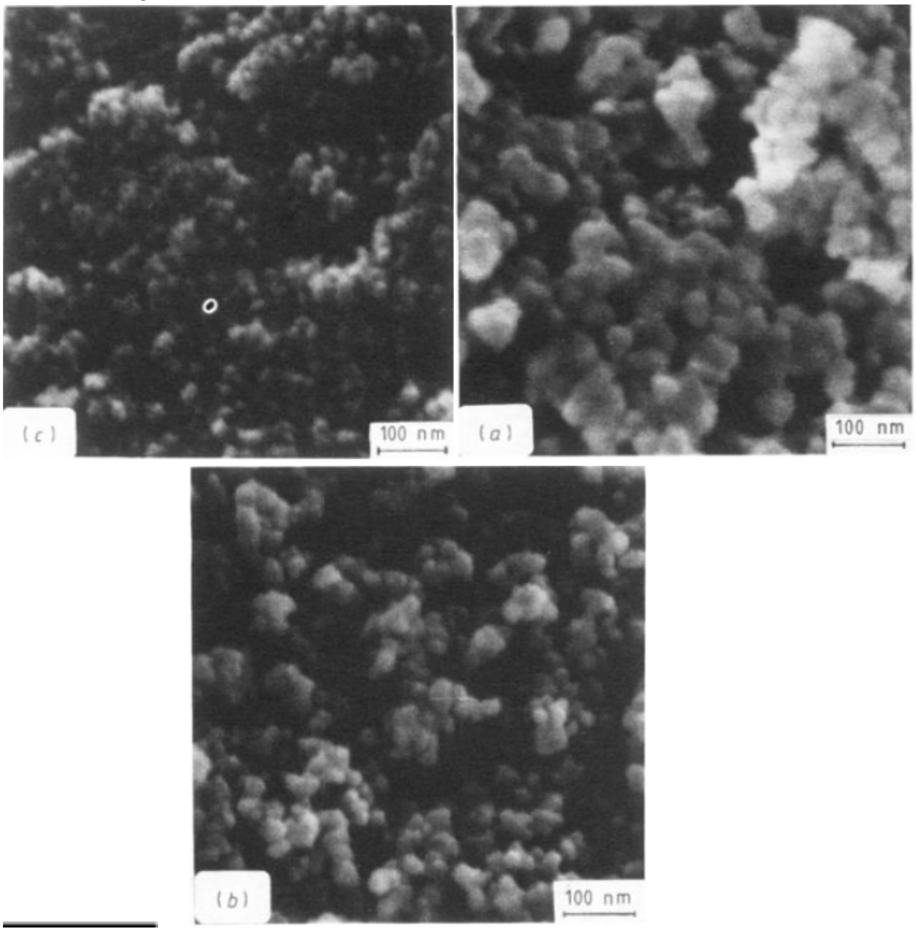
It Was used on the Mars Pathfinder Sojourner rover and currently is under the mission of catching a piece of a comet on the Stardust mission.It has been used to insulate the batteries of the 2003 Mars Exploration Rovers.

2. Structure

Aerogels consist of a complicated cross-linked internal structure of chains of the aerogel constituent molecules with a large number of air-filled pores that take up most of the volume. Observations by scanning electron microscopy and transmission electron microscopy led to the following conclusions about the structure of an aerogel (of density 0.23 gm cm^{-3}) studied by J L Rousset et al.

Primary chains, 30-50 A in diameter, form the substructures of grains whose size varies from 100 to 500 A, depending on density. The grains form large-scale aggregates, leading to pores on scales exceeding 1000 A**.**

Most aerogels have a structure that is similar to that described, with changes only in scale.



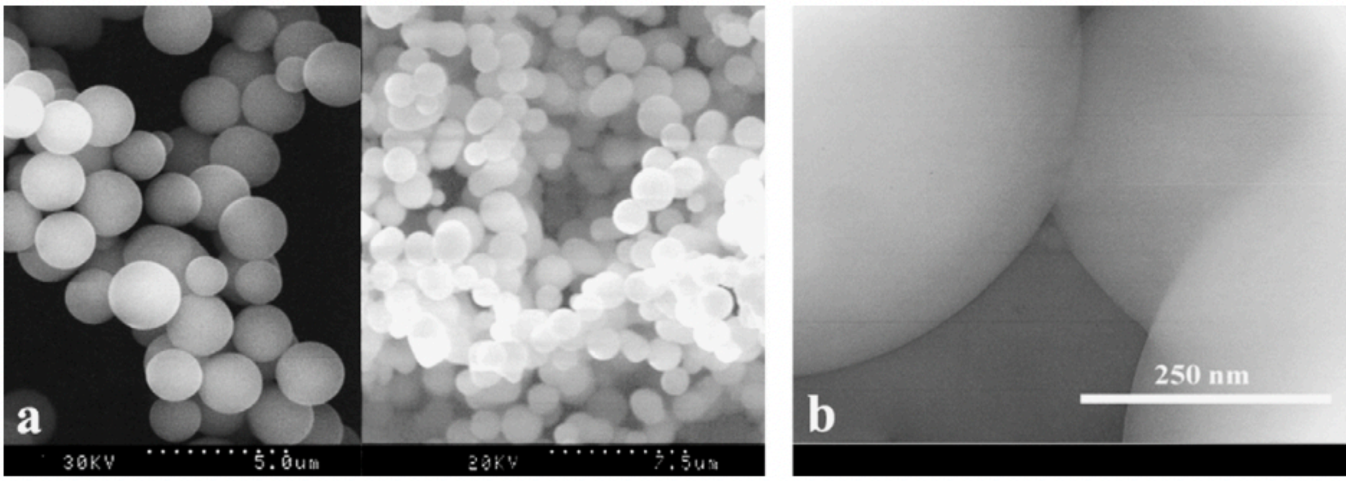


Fig. 12 – (a) SEM; (b) TEM picture, showing the pore characteristics of silica aerogels.

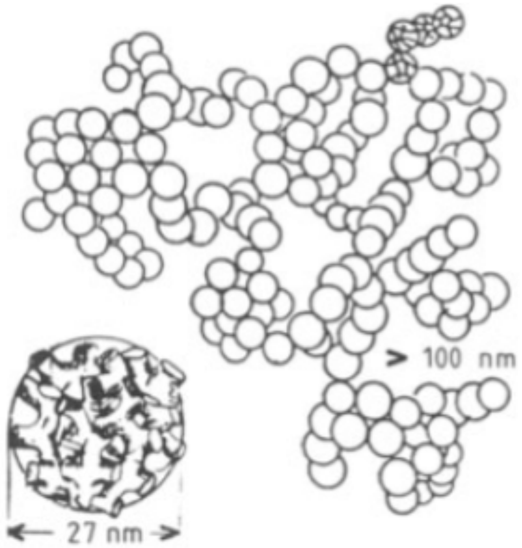


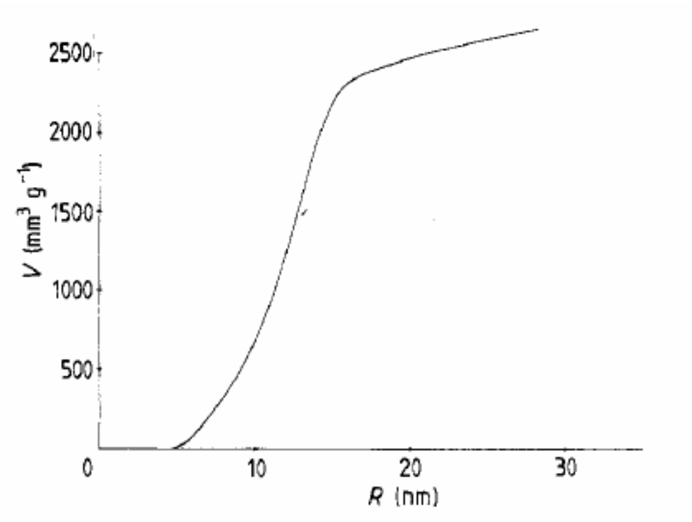
Figure 4. Sketch of the aerogel structure deduced from electron microscopy.

3

Information on pore volume and pore size distribution is determined by “Thermoporometry”. From the results of J L Rousset et al, to be consistent with the measured overall aerogel density of 0.23 g cm-3 for the given sample, 27% of the total pore volume must correspond to pores of radius larger than 350 A. This amount of macroporous volume is close to that estimated from SEM pictures.

Table 1. Values of $\rho(r)$ and the percentage of inter-grain porous volume.

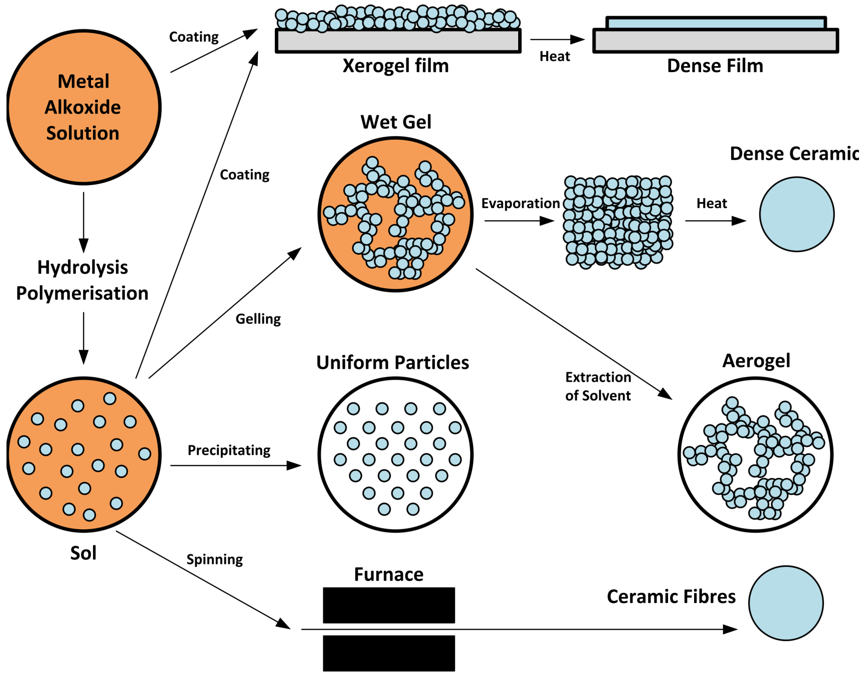
Aerogel density (g cm^{-3})	Density in grains (g cm^{-3})	Diameter $2r$ of grain, SEM (Å)	Diameter ($2\sqrt{5}\xi$) of fractal grain, SANS (Å)	Inter-grain porous volume (%)
0.36	0.89	130	179	75
0.23	0.60	270	360	67
0.107	0.395	500	1180	77



3. Synthesis of Aerogels

3.1 Sol-Gel Process

Aerogels are commonly synthesized by the Sol-gel process. The Sol-gel process could be described as the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid. The formation of aerogels, in general, involves two major steps, the formation of a wet gel, and the drying of the wet gel to form an aerogel. Silica aerogels are generally prepared from silicon alkoxide precursors. The most common of these are tetramethyl orthosilicate (TMOS, Si $(OCH_3)_4$),



and tetraethyl orthosilicate (TEOS, Si $(OCH_2CH_3)_4$). However, many other alkoxides, containing various organic functional groups, can be used to impart different properties to the gel. The initial step in the formation of aerogels is hydrolysis and condensation of alkoxide. As condensation reactions progress the sol will set into a rigid gel. The kinetics of the above reaction is impracticably slow at room temperature, often requiring several days to reach completion. For this reason, acid or base catalysts are added to the formulation. These catalysts speed up the hydrolysis of silicon alkoxide. In acidic environments, the oxygen atom in Si-OH or Si-OR is protonated and H-OH or H- OR are good leaving groups. The electron density is shifted from the Si atom, making it more accessible for reaction with water. In basic environments, nucleophilic attack by OH^- occurs on the central Si atom. The amount and type of catalyst used to play key roles in the final aerogel product's microstructural, physical and optical properties. For example, aerogels prepared with acid catalysts often show more shrinkage during supercritical drying and are less transparent than base-catalyzed aerogels. As the reaction progresses, the sol reaches the gel point, that is, the point in time at which the network of linked oxide particles spans the container holding the Sol. At the gel point, the Sol becomes an Alcogel.

Typical acid or base-catalyzed TEOS gels are often classified as "single-step" gels, referring to the "one-pot" nature of this reaction. A more recently developed approach uses pre-polymerized TEOS as the silica source. Pre-polymerized TEOS is prepared by heating an ethanol solution of TEOS with a sub-stoichiometric amount of water and an acid catalyst. This material is redissolved in ethanol and reacted with additional water under basic conditions until gelation occurs. Gels prepared in this way are known as "two-step" acid-base catalyzed gels. These slightly different processing conditions impart subtly, but important changes to the final aerogel product. Single-step base-catalyzed aerogels are typically mechanically stronger, but more brittle, than two-step aerogels

While two-step aerogels have a smaller and narrower pore size distribution and are often optically clearer than single-step aerogels.

The final, and most important, process in making silica aerogels is supercritical drying. This is where the liquid within the gel is removed, leaving only the linked silica network. The process can be performed by venting the ethanol above its critical point (high temperature-very dangerous) or by prior solvent exchange with CO_2 followed by supercritical venting (lower temperatures-less dangerous). The alcogels are placed in the autoclave (which has been filled with ethanol). The system is pressurized to at least 750- 850 psi with CO_2 and cooled to 5-10 degrees C. Liquid CO_2 is then flushed through the vessel until all the ethanol has been removed from the vessel and from within the gels. When the gels are ethanol-free the vessel is heated to a temperature above the critical temperature of CO_2 (31 degrees C). As the vessel is heated the pressure of the system rises. CO_2 is carefully released to maintain a pressure slightly above the critical pressure of CO_2 (1050 psi). The system is held at these conditions for a short time, followed by the slow, controlled release of CO_2 to ambient pressure. Under these conditions, the network structure is retained and a gel with large pores is formed. The density of the resulting aerogel will be very low generally somewhere around 0.1 g/cm^3. If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. This supercritical besides being a critical step in the production of aerogels is also one of the major obstacles in the mass production of aerogels. This process is both time-consuming (several days) and costly.

3.2 PREPARATION OF CARBON AEROGELS

The above-mentioned method of preparing silica aerogels is not very successful in the case of carbon aerogels mainly due to the effects of steric hindrance in tetra alkyl ethers. Instead, a variant of the Sol-gel process is used. The precursor that is generally used in the synthesis of carbon aerogels is the resorcinol-formaldehyde solution. Polycondensation of resorcinol with formaldehyde in aqueous solutions leads to gels that can be super critically dried with CO_2 to form organic aerogels which are called resorcinol-formaldehyde (RF) aerogels. Carbon aerogels can be obtained by pyrolysis of resorcinol formaldehyde aerogels in an inert atmosphere.
Carbon aerogels are considered to be ideal electrode materials for supercapacitors and rechargeable batteries. However, they also have the same disadvantage as silica aerogels as their preparation involves supercritical drying. Another disadvantage is the high cost of resorcinol.

STRUCTURE

the crystal structure of SiO_2 has been determined using single-crystal methods. The structure consists of layers of the composition of Si and O . Silicon dioxide (SiO_2) is a covalent molecule with four oxygen atoms connected to each silicon atom and two oxygen atoms bonded to each silicon atom in a **tetrahedral structure**. Silicon dioxide has a large structure with an eight-membered ring produced by the arrangement of alternate oxygen and silicon atoms.

CRYSTALLOGRAPHIC DATA:-

CELL LENGTH A -5.136

CELL LENGTH B -5.136

CELL LENGTH C -5.136

CELL ANGLE α -121.022°

CELL ANGLE β -121.022°

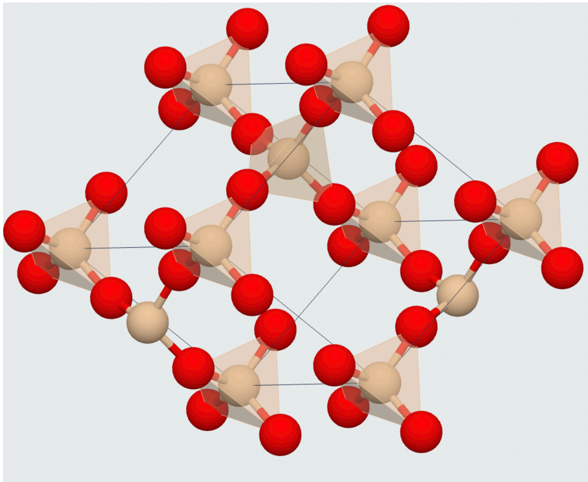
CELL ANGLE γ -88.239°

CELL VOLUME -94.262 $Å^3$

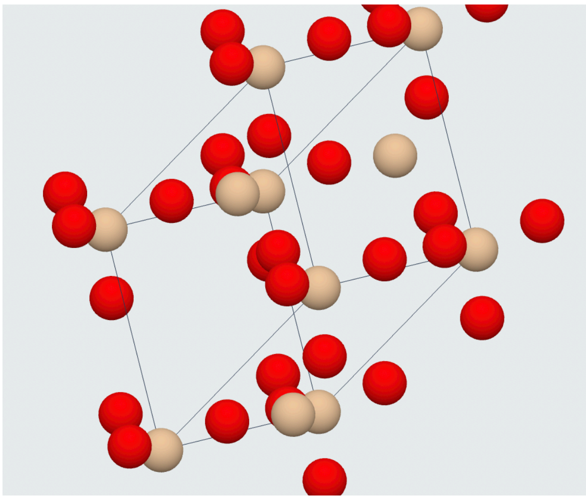
CRYSTALLINE STRUCTURE

The most common type of silicon alkoxides used for making silica gels are tetraethoxysilane, abbreviated “TMOS”, and tetraethoxysilane abbreviated “TEOS”. Both are tetrahedral, non-polar molecules. TMOS is also correctly called tetramethyl orthosilicate, where “orthosilicate” means SiO44-.t

The four methods group bound to silicon are evenly spaced in three dimensions, resulting in a net cancellation of dipole moments. This makes tetraethoxysilane (TMOS) NON-POLAR, AND THUS immiscible with water.



Structure



cubic structure

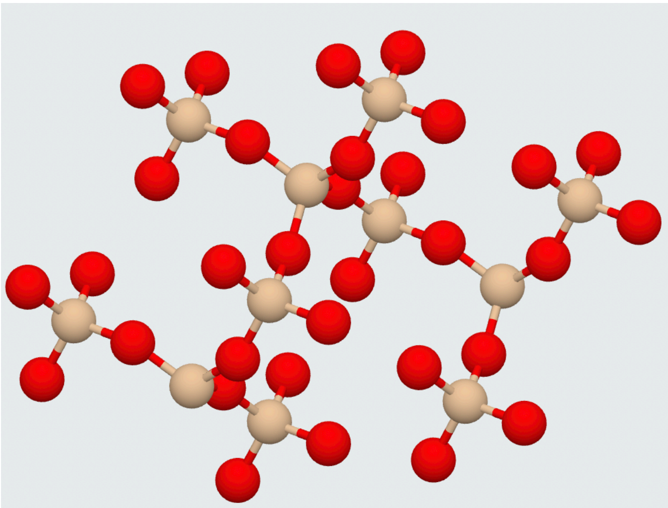
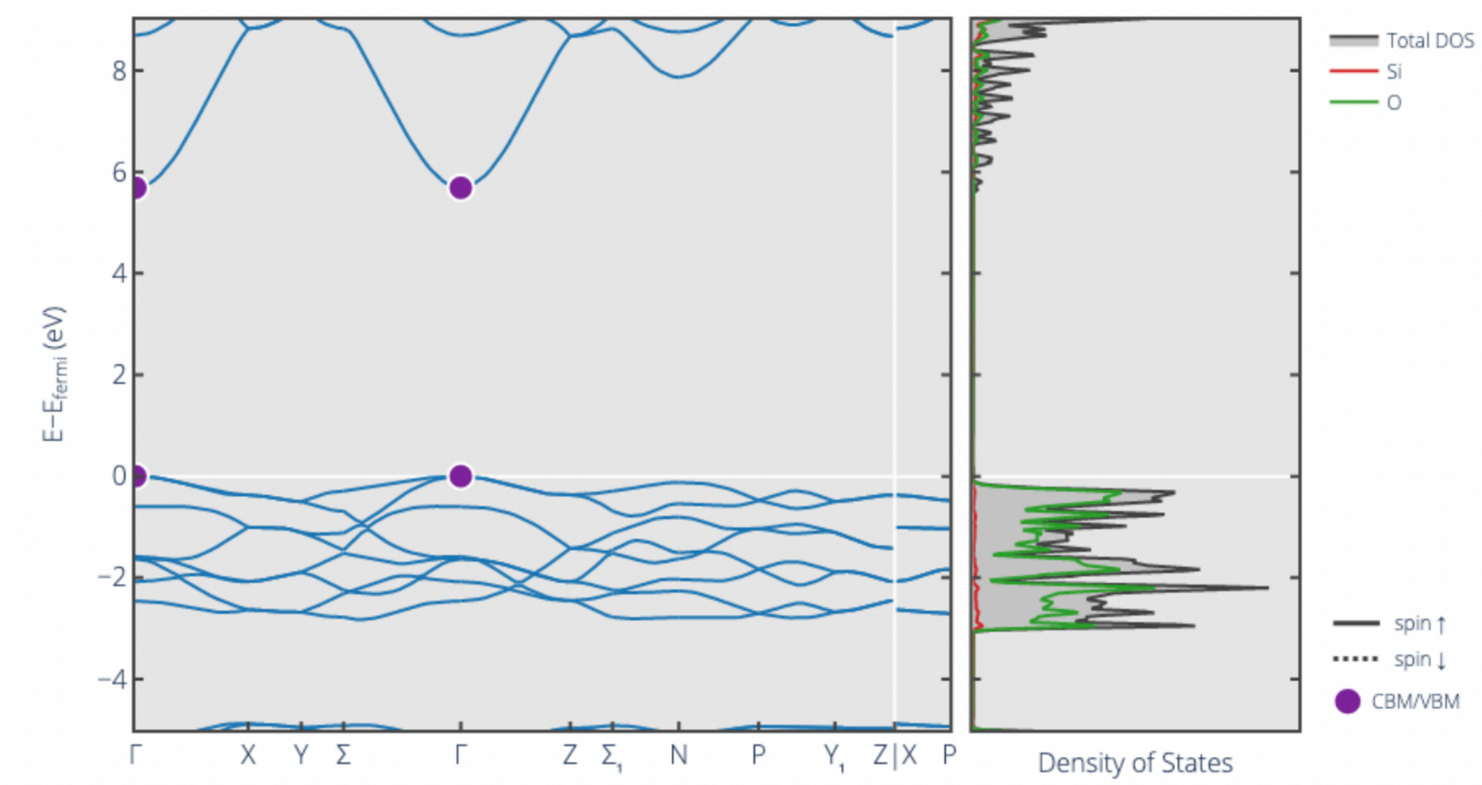


FIGURE SHOWING BONDS BETWEEN SI & O

BAND STRUCTURE AND DENSITY STRUCTURE



HISTORY

The invention of Aerogels is credited to Dr Samuel Stephens Kistler, a chemical engineer, professor, and former Dean of the University of Utah's School of Engineering. Kistler first surmised the idea of replacing the liquid phase of a gel with gas, with a minimum loss of volume. With this

hypothesis, Kistler produced silica aerogels. As a professor of chemistry at the University of Illinois, Kistler was a consultant for DuPont, Rayon, and the Monsanto Company in their material sciences division. During Dr Kistler's time at the Monsanto Company, aerogels were commercially marketed under the name Cancel. Cancel was advertised as a low-weight, low-volume alternative to traditional insulators for gas containers, refrigeration insulation, and steam lines and pipelines to reduce losses through the pipe.
Figure 1 on the right shows an advertisement for Santocel, a trademark for Silica Aerogel, under the Monsanto Company
A new method of production was developed in the late 1970s by researcher Stanislaus Teichner at Universite Claud Bernard, Lyon.
Working with his graduate students, they applied the sol-gel method of synthesizing aerogels. This was more efficient and less time-consuming than the traditional solvent-swapping method developed by Kistler. This allowed for innovations to be made within the field of aerogels for thermal insulation, waste management, molten metals, optics, electronic devices, capacitors, pesticides, and cosmic dust collection.

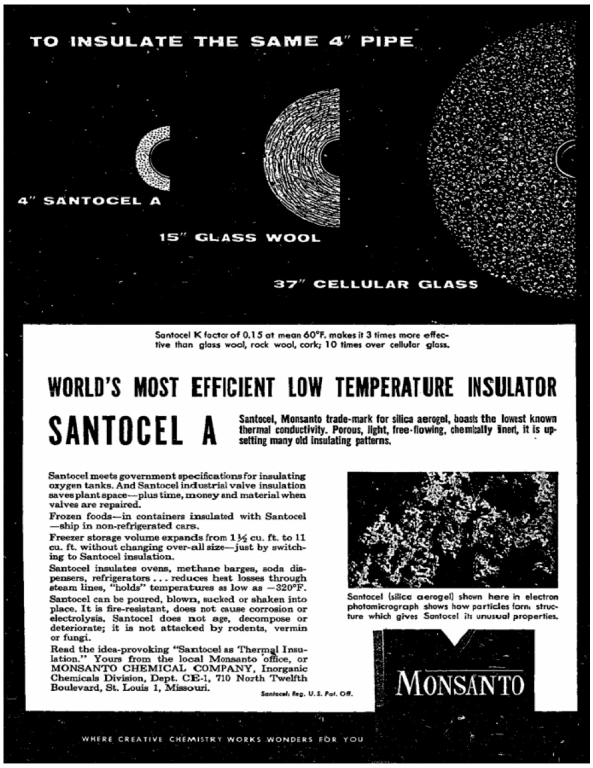


Figure 1: Advertisement for Santocel, a trademark for Silica Aerogel, under the Monsanto Company

PHYSICAL PROPERTIES

Strength, T_s, (kPa)	14-16
Density, ρ (g/cm^3)	0.08–0.10
Young's Modulus, E (MPA)	0.1 - 10
Specific Heat Capacity, λ (W/m-K)	0.01 – 0.04
Thermal Conductivity, c_p (J/g-K)	0.7–1.15
Melting Point, M_p (°C)	1700
Boiling Point, Bp (°C)	2230

Density

Volume shrinkage of the aerogels is calculated from the volumes of the hydrogel and aerogel. Two different terms are used to characterize silica aerogels: bulk density and skeletal density.

Bulk density ($?_b$) is defined as the ratio of the aerogel's mass to its volume.

The texture of the solid part of aerogels is made of ultra-fine particles. The skeletal density of these particles is supposed to be very close to that of the bulk solid.

Optical properties

In many procedures, the resulting silica aerogels are transparent. This is an unusual property for a porous material. The reason for this relatively rare combination of traits arises because the aerogel microstructure has a scale small compared to the wavelength of light. Transparency occurs because there is a small amount of scattering in the visible, the scattered light has a relatively isotropic angular distribution and exhibits little multiple scattering. This behaviour can be described by the Rayleigh scattering theory. Rayleigh scattering is characterized by the isotropic scattering of the vertically polarized incident light, an intensity that varies with scattering angle as $\cos^2 ?$ for horizontally polarized

In many applications, their transparency plays an important role. This remark attracted the attention of scientists working in high-energy physics with charged particles and looking for the construction of a new type of solid state. Due to their very high thermal insulation properties and their optical transparency in the visible region, they were proposed for double-plane windows. Thus, multiple efforts have been undertaken to improve this characteristic of silica aerogels. Initially, various physically oriented approaches were taken for solving this problem, such as investigation of the influence of the drying process, of water adsorbed to Si-OH groups, or absorbed organic components. Heating the aerogels improves their transparency due to the desorption of water and burning of organic components. Also, the sol-gel process parameters and the type of silation agent greatly influence the optical properties of aerogels. It has been shown that the two-step synthetic method resulted in more transparent aerogels than those obtained by one-step synthesis. Bulk scattering can be minimized by the selection of optimal synthesis parameters. Recently, synthesized new aerogels with a refractive index larger than 1.03 by introducing dimethyl-formamide (DMF), as a solvent in the sol-gel process. At low temperatures, the radiative component of thermal transport is low, but at higher temperatures, radiative transport becomes a dominant mode of thermal conduction.

An attempt to calculate the total thermal conductivity from the sum of these three modes can prove difficult because the modes are coupled. For measurement of the thermal conductivity, a Vacuum Insulation Conductivity Tester – VICTOR – may be employed.

Hydrophobicity

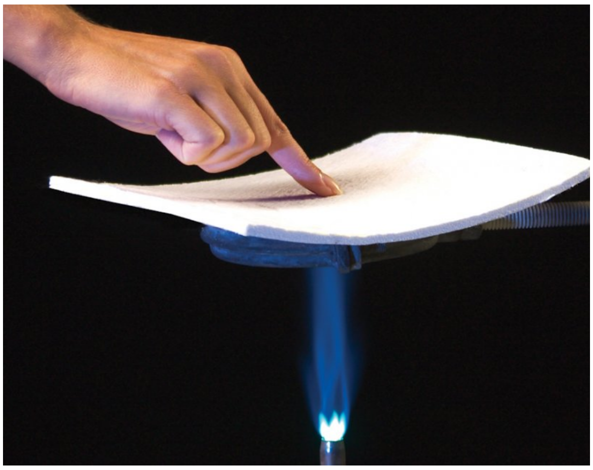
Silica aerogels can either be hydrophilic or hydrophobic, depending on the conditions during synthesis. The silanol polar groups Si-OH present in the aerogel structure are the main source of hydrophilicity because they can promote the adsorption of water. Generally, aerogels synthesized by unmodified hydrolysis and condensation of alkylorthosili- cates and dried by high-temperature SCD are hydrophobic, and those dried by CO_2 are hydrophilic. This difference is due to the different surface groups formed during the SCD pro- cess. LCD results in hydroxyl groups (–OH) on the surface resulting in hydrophilic aerogels. HTSCD allows for the reaction of the surface hydroxyl groups with the solvent to form methoxy groups $(–OCH_3)_X$ and thus results in hydrophobic aerogels.

A second approach for increasing the hydrophobicity is the modification of the aerogel surface after drying. The surface of hydrophilic aerogels can be modified by a reaction with gaseous methanol (Kun-Hong Lee et al., 1995).

The hydrophobicity of the aerogels was tested by measuring the contact angle (?), of a water droplet with the aerogel surface using the formula,

3.4. Thermal conductivity

Because of porosity and nanometer pore size, silica aero-gels are highly insulating materials with a thermal conductivity lower than still air. Kistler demonstrated that an aerogel's thermal conductivity is in the order of 0.02 W/mK at ambient pressure in air and 0.01 W/mK when evacuated.



Because silica aerogels have a very small (~1–10%) fraction of solid silica, thus exhibit a lower solid conductivity and transmit lower thermal energy.

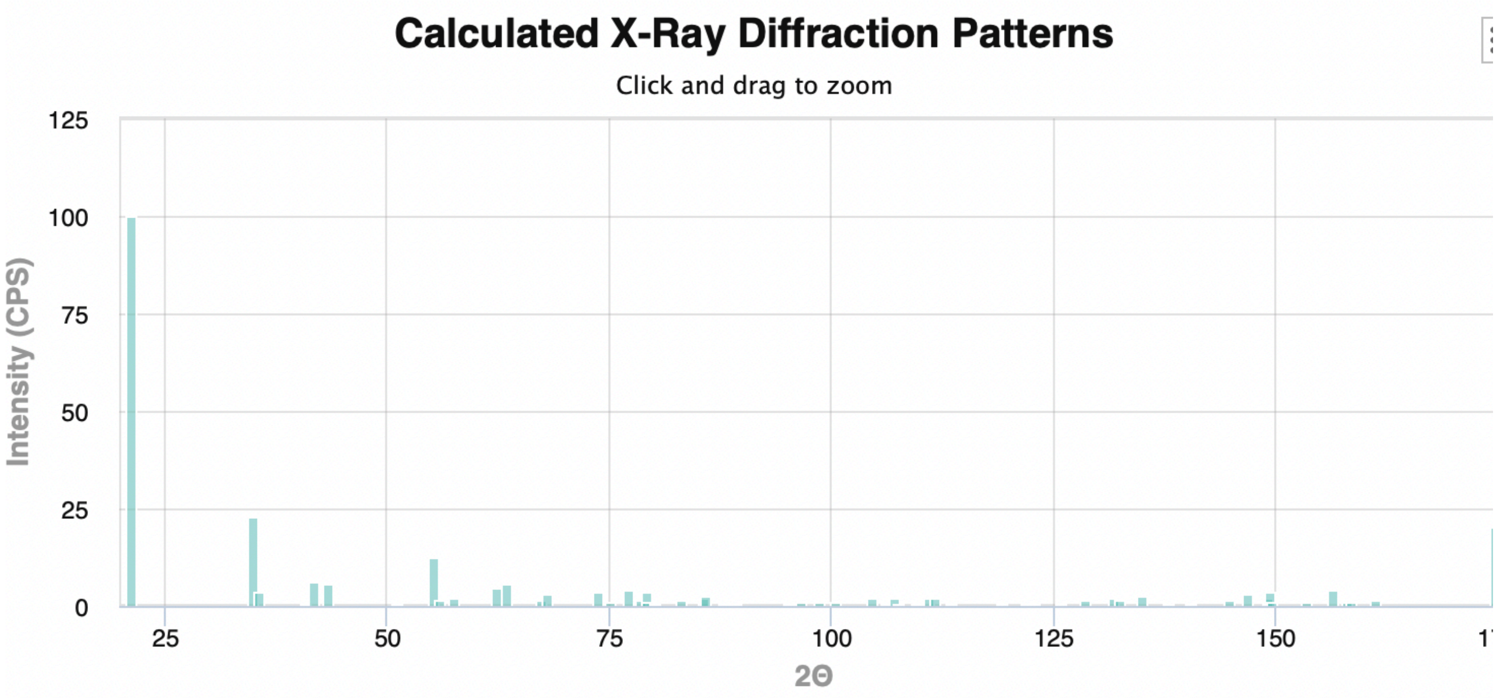
Gases are also able to transport thermal energy through the aerogel. The pores of silica aerogel are open and allow the passage of gas through the material.

The final mode of thermal transport through silica aero-gels involves infrared radiation. An important parameter that influences this transfer route is the optical thickness of the aerogel.

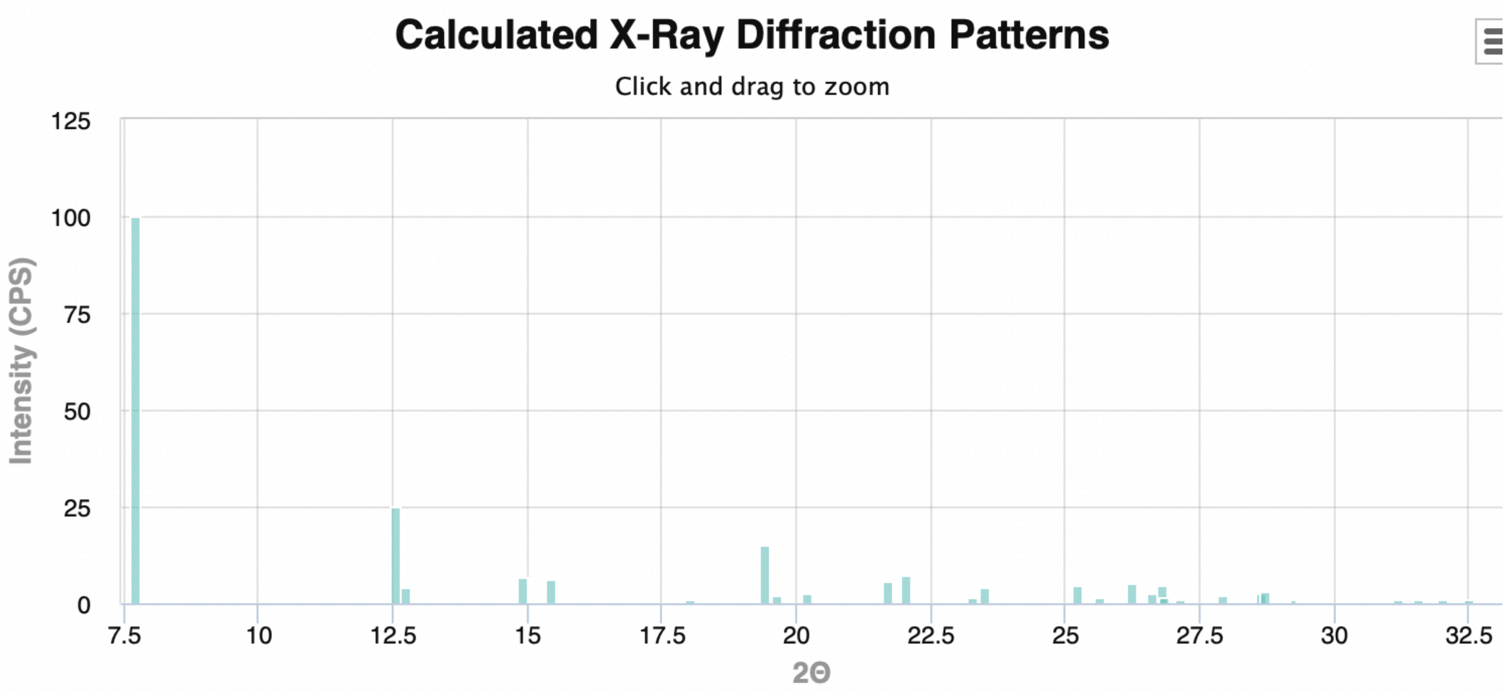
ANALYSIS OF SiO2

X-RAY ANALYSIS

radiation source- Cu

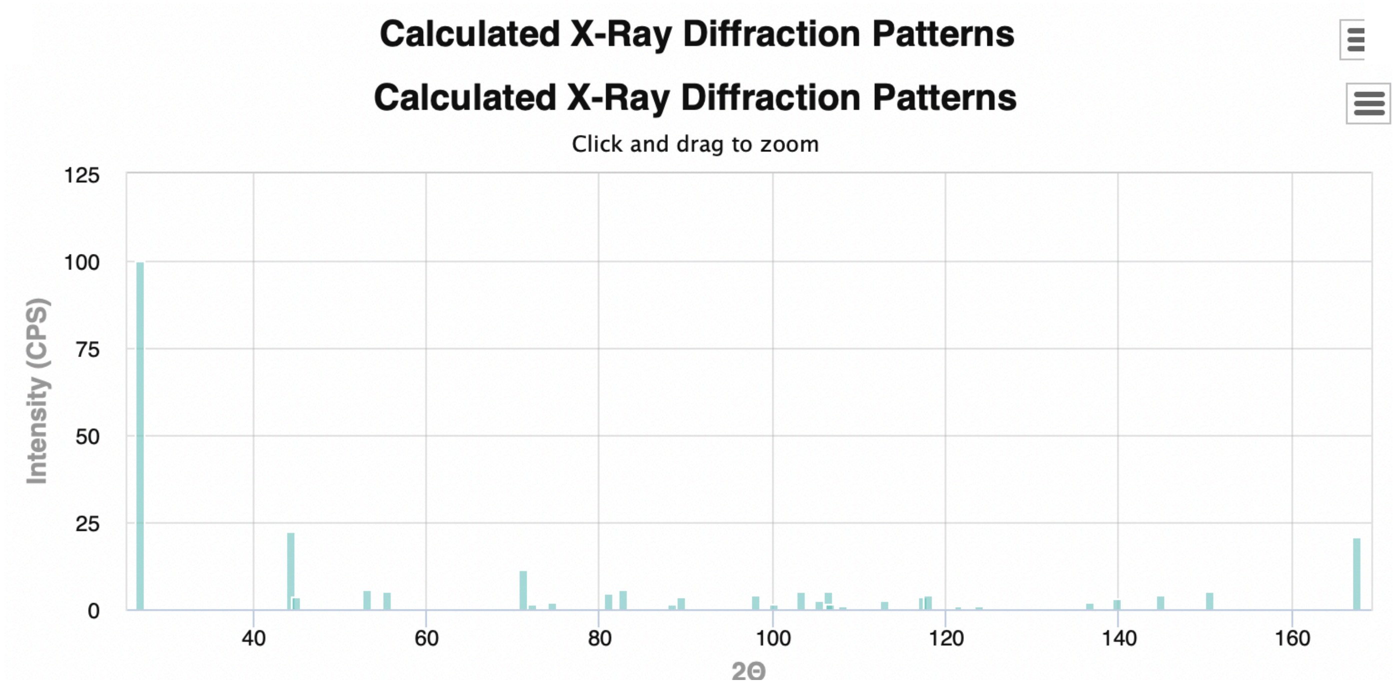


radiation source Ag



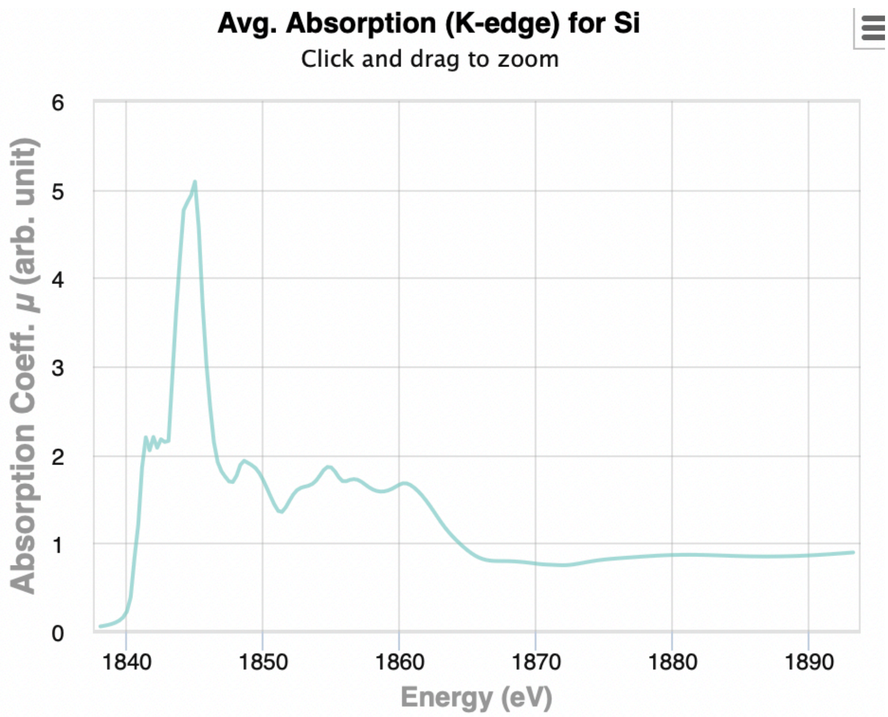
Caption

radiation source- Molybdenum

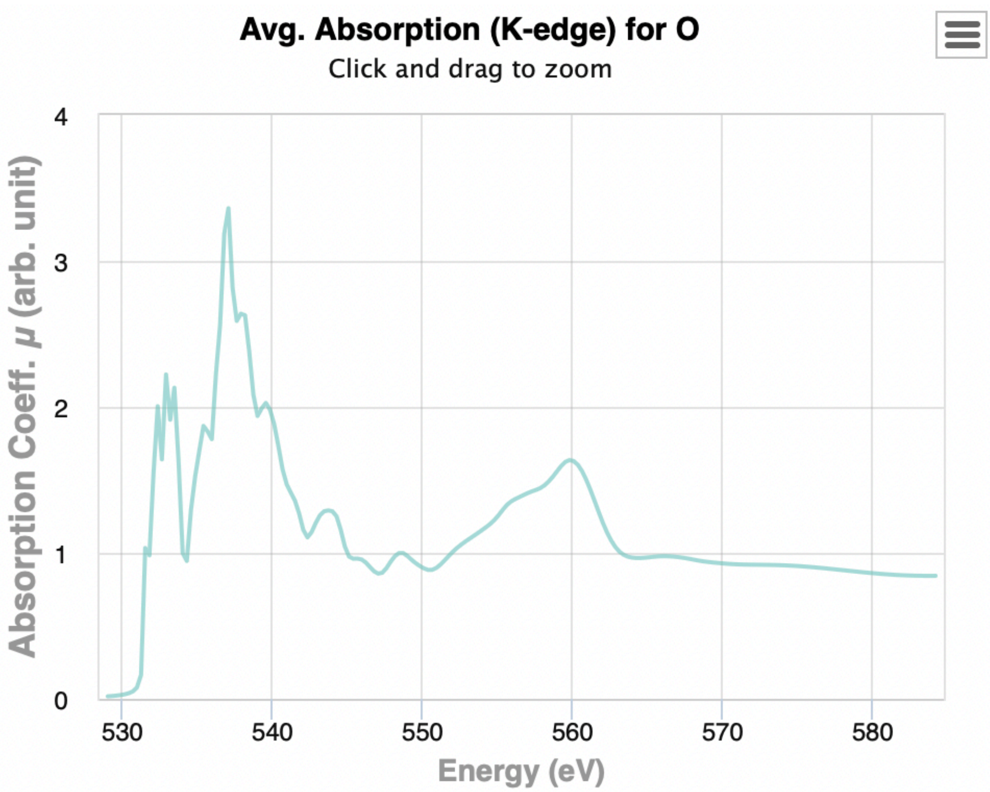


radiation source - Iron

X-RAY ABSORPTION SPECTRA
FOR SILICON-

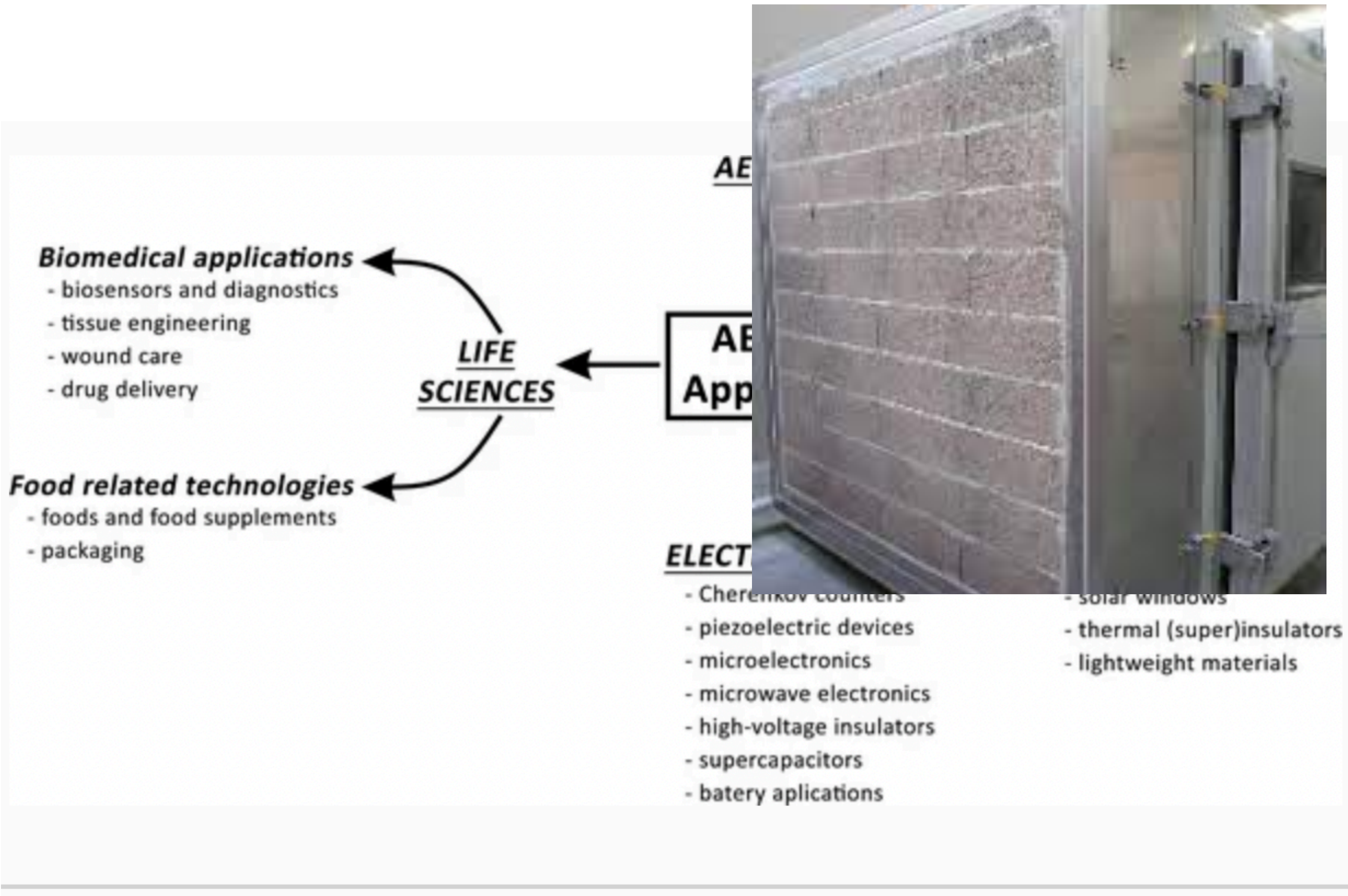


FOR OXYGEN-



APPLICATIONS

In space



In space, aerogels have already been used as thermal isolation material in the Mars Rover of the Pathfinder mission. NASA used aerogel to insulate the electronics on the intrepid Sojourner from the chisel cold of the Martian night. A disadvantage of conventional aerogels is their brittleness and small mechanical stability. Recent developments demonstrate, however, that the mechanical characteristics of aerogels can be improved significantly by using inorganic and organic material combinations (e.g. silicate/Polyurethane) substantially. Therefore, in the future, aerogels may find applications as high-strength, ultra-light, thermally insulating structure material in space.

In Refrigerators

Aerogels are a more efficient, lighter-weight, and less bulky form of insulation than the polyurethane foam currently used to insulate refrigerators, refrigerated vehicles, and containers. And, they have another critical advantage over foam. Foams are blown into refrigerator walls by chlorofluorocarbon (CFC) propellants, the chemical that is the chief cause of the depletion of the earth's stratospheric ozone layer. Replacing chlorofluorocarbon-propelled refrigerant foams with aerogels could help reduce this toll.

In Housing, Skylights, Windows

Factors which make aerogels suitable for use in housing: (i) Made of inexpensive silica, aerogels can be fabricated in slabs, pellets, or almost any shape desired and have a range of potential uses (ii) By mass or by volume, silica aerogels are the best solid insulator ever discovered. Aerogels transmit heat only one hundredth as well as normal density glass.

Associated problems:

•(i) Aerogels are friable, i.e. they are prone to shattering like glass.

- (ii) Aerogels are hygroscopic in nature and on absorbing moisture; they will usually cause a structural change of contraction etc. and deteriorate. After the
first rain, they would turn to sludge and ooze down the side of the house

- (iii) Aerogels are transparent but they are not transparent enough to be used in
double-paned windows.

- (iv) Despite its superior efficiency, the cost of production of Aerogel panes will be
pretty high compared to other existing cheaper alternatives.

Proposed solution:

It has been shown that producing aerogel in a weightless environment can produce particles of more uniform size and reduce the Rayleigh scattering effect in silica aerogel, thus making the aerogel less blue and more transparent. Sandwiched between two layers of glass, transparent compositions of aerogels make possible double-pane windows with high thermal resistance. Furthermore, it is also possible to make aerogels hydrophobic by chemical treatment.

I*n Clothing, Apparel, Blankets*

Aspen Aerogels Inc. of Marlborough, Massachusetts has produced a Spaceloft product, an inexpensive, flexible blanket that incorporates a thin layer of aerogel embedded directly into the fabric. Spaceloft is relatively inexpensive, flexible, hydrophobic, and breathable. It is also three times more effective than the best commercially available clothing insulation. Jackets made out of this material are intended for wear in extremely harsh conditions and activities, such as Antarctic expeditions. As the price of Spaceloft comes down with mass production, it is expected to be more widely used in everyday winter clothing. Recently, NASA's Johnson Space Center used Spaceloft to construct mittens as a precursor to space gloves for Mars exploration.

Caption

Another type of aerogel is organic, which is made of carbon and hydrogen atoms. Organic aerogels are stiffer and stronger than silica aerogels and are measurably better insulators. Organic aerogels have an extremely high thermal resistance (six times higher than fibreglass) and can be converted to pure carbon aerogels while still retaining many properties of the original aerogel - in addition to becoming electrically conductive.

Aerogels: optical properties and applications

Aerogels show very interesting optical properties. E.g. we take silica aerogels. They are transparent since they are made of the same material as glass. It has a bluish appearance off reflected light and causes reddening of transmitted light. These effects can easily be explained using Rayleigh scattering effects.

AEROGELS TODAY

NASA prominently uses aerogels for its outer space purposes. Polymer-enhanced Aerogels have been developed by NASA for their low density and thermal conductivity. “These polymer-enhanced aerogels offer the same insulation properties as typical aerogels and can be translucent. They share the same positive attributes of silica aerogels and are much less fragile.” NASA also used aerogel for the thermal insulation of space suits and the Mars Rover.

The Lawrence Livermore National Laboratory has developed a method of a Capacitive Deionization process that purifies salt water (salt content between 800 ppm-1200ppm) between two carbon aerogel electrodes. This method uses up to 10 times less energy than conventional electrolysis methods.

4

Caption

Kistler Aerogel Jackets – by SUPPLIED. A Kickstarter uses a thin insulating layer of aerogel fabric to provide resistance from cold temperatures. Kickstarter claims to resist temperatures as low as 200 °C. Unfortunately, reviews on the product page on its Kickstarter page are mostly negative due to the company’s poor customer service and long, usually inaccurate shipping service.

FUTURE AHEAD

Current massive wall-building materials can be characterized by having either low thermal conductivities and thus low bulk densities and low compression strength or high compressions strength, high bulk densities and high thermal conductivities. In this paper, the first results of a research project are presented, in which a new aerogel-based construction material is developed that exhibits extraordinary heat-insulating and load-carrying properties. By embedding silica aerogel granules in a high-strength cement matrix “High-Performance Aerogel Concrete” is developed, which combines the benefits of conventional concrete (compressive strength, unlimited moldability) with the properties of a

Caption

heat-insulating material. So far, various mixtures were examined in terms of their compressive strength and thermal conductivity. The first results are very promising with a compressive strength between 3.0 MPa and 23.6 MPa and thermal conductivities between 0.16 W/(mK) and 0.37 W/(mK).

CONCLUSION

This paper provides a comprehensive review of the synthesis, structure, properties and characterization of silica aerogels. Aerogels show great promise for use in a variety of technological areas where special structure and physical properties are required. Substantial progress has been made in the development, processing and characterization of aerogel materials over recent years. Special attention has been paid to the use of inexpensive precursors such as sodium silica (water glass) and the drying technology to make the production commercial. Silica aerogel synthesis with various materials and process conditions and also the properties and method of determination are reviewed and summarized in this paper.

Initially synthesized in 1936, Aerogels are a relatively new material that has seen their production methods and commercial applications shift in the 80 years since their discovery. Innovation in replacing silica with carbon-metal alloys and in a variation of the structure has seen a vast improvement in its material properties. Despite these innovations, aerogels have not found a consistent market outside of the aerospace industry. Chemical modification methods and ambient pressure drying aim to reduce the cost of production and make aerogels more competitive with other materials.
The global market of aerogels is expected to grow from 63 million dollars in 2020 to 1000 million dollars and beyond by 2035.

Acknowledgement

Dr MUNENDRA JAIN

physics professor

SVKM, STME

NMIMS INDORE

REFERENCES

1) https://materialsproject.org/materials/mp-546794/
2) https://www.sciencedirect.com/
3) https://www.researchgate.net/
4) https://pubs.acs.org/
5) https://scholar.google.com/