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Optimized synthesis of ambient pressure dried thermal insulating silica aerogel powder from non-ion exchanged water glass

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ABSTRACT

Silica aerogels are considered as promising materials for future energy saving buildings, however, their reliability remains questionable as commercially available aerogels can show relatively high standard deviations e.g. 22.2 ± 1.4 mW m^{-1} K^{-1}. Therefore a synthesis protocol for silica aerogel powder with thermal conductivities having extremely reduced standard deviations was designed, compatible with mass production, i.e. reduced use of solvents and hydrophobization agents. Silica sols were prepared from non-ion exchanged water glass, while a combined solvent exchange, silylation and washing out of sodium ions was carried out using a hexane/trimethylchlorosilane/isopropyl alcohol solution with a molar ratio trimethylchlorosilane/pore water of only 0.11. The hexane amount was reduced 35 times compared to typical processes in literature. The aerogel powder was finally dried at ambient pressure at 150 °C. No notable shrinkage was observed for 8 wt% silica aerogel samples, having a thermal conductivity of 25.4 mW m^{-1} K^{-1} with a standard deviation of only 0.1. The 6 wt% silica aerogels had a thermal conductivity of 23.4 mW m^{-1} K^{-1} with a standard deviation of 0.3, but had shrunken 36%. By replacing trimethylchlorosilane with hexamethyldisiloxane, aerogels having a thermal conductivity of 22.4 mW m^{-1} K^{-1} with a standard deviation of 0.3 were obtained.

1. Introduction

Regarding climate change, buildings are responsible for 40% of energy consumption and 36% of CO_2 emissions in Europe according to the European Commission [1]. Future buildings have to be constructed according to the highest standards of low energy consumption by 2020, which is difficult to achieve with conventional construction materials [2, 3]. Silica aerogels are obtained with low densities (< 0.05 g cm^{-3}), high specific surface area (> 1000 m^2 g^{-1}), high porosity (90–99.8%) and low thermal conductivity (< 20 mW m^{-1} K^{-1}) [4]. They can then be seen as the perfect candidates to meet these energy requirements. However, the reliability of the available aerogels in term of thermal conductivity is often unsure as the standard deviation is either not given [5-7] (lab scale) or rather high [8, 9] (commercially). Furthermore the high cost price often prevents these materials to be applied on a wide scale, especially in low-cost matrices, like cement, plaster or other building products. Another issue is that during the synthesis, toxic components e.g. tetramethyl orthosilicate (TMOS), high amounts of solvents, high pressures and temperatures are needed, resulting in a not very environmentally friendly material [10-15]. The use of cheap precursors, low amounts of solvent and hydrophobization agent, and no supercritical drying [16-20] help to obtain greener aerogels for reasonable prices. Water glass, an aqueous solution of sodium silicate, is therefore a relevant precursor choice and can moreover be obtained out of building waste material [21]. Sodium silicate is about four times less expensive than tetraethyl orthosilicate (TEOS), but contains sodium ions and gives less homogeneous gels compared to silica alkoxides [22]. This is commonly solved by first ion exchanging the sodium ions of the water glass with hydrogen ions via a cation exchange resin to obtain silicic acid having a pH typically around 2 [23-27]. A base like ammonia or diluted sodium hydroxide is then added to this silicic acid until a pH of 3.5–5 is reached [18, 28]. Silanol groups from the silicic acid bond with each other (condensation) forming siloxane bridges, forming a stable suspension of colloidal solid nanoparticles in water, also called the sol [27, 29]. Gelation then starts as the sol condensates further and more siloxane bridges got formed, resulting in a network. Although homogeneous gel structures can be obtained, the disadvantages of the ion exchange method are the unavoidable presence of residual sodium ions in the low limit, the environmental costs of recovering the ion exchange resin [30] and its unknown impact on the final cost of the material [31]. In case the sodium ions were not exchanged out of the water glass, which is basic in nature having a pH

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higher than 12, an acid e.g. hydrochloric or nitric acid needs to be added to neutralize the sodium silicates so that hydrolysis will occur and silanol groups will form [29, 32, 33]. Homogeneous gels can be obtained at a pH below 6, whether or not a salt (sodium) is present [27]. However, in neutral or alkaline conditions and if the silica sol contains substantial amounts of salts, a white precipitate (rapid coagulation) is formed or in some cases a white opaque gel due to partial precipitation before gelation [27, 34].

Schwertfeger et al. [35] stated that the sol-gel process can be considered as the step where the properties of the final aerogel are determined, which is logical as an aerogel is obtained when the wet gel almost does not shrink irreversibly during drying and therefore maintains the same porous structure. A network built of thin backbones and mesopores (2–50 nm) poorly conducts heat both through the solid and gas phase, and is therefore desired for good thermal insulation properties [4]. However, a network consisting of thin chains is more likely to collapse, resulting in an irreversible shrunken and collapsed structure, called xerogel [4, 27] with a high density, small pore volume and high thermal conductivity. Gels can be aged to allow further polymerization (coarsening) resulting in stronger network. However, collapse (syneresis) and air bubble formation can still occur destroying the pore structure. Aging at room temperature takes considerably longer to obtain the same strength and stiffness than when performed at higher temperatures, but it is the safest way and also results in the strongest gels [36]. In the case of aerogel powders, contrary to monoliths, the formation of air bubbles is not a real issue.

In this study, ambient pressure drying (APD) is preferred to supercritical drying as it does not require an autoclave, which operates at high pressures and temperatures and limits the sample size to less than its volume. A silica aerogel can be obtained out of APD only through surface modification and solvent exchange [14, 15, 37-39]. Both procedures make sure that the gel does not collapse when the pore liquid evaporates and leaves the gel during drying at ambient pressure by minimizing the capillary pressure. The surface modification, also called silylation, replaces the silanol groups on the backbone surface with methyl groups, creating a (super)hydrophobic gel. Without this treatment, the gel network would shrink during APD as silanol groups get close to each other, react and form siloxane bridges, resulting in a xerogel. Methyl groups on the other hand, slightly repel each other and induce a spring back effect or reversible shrinkage. However, the pore liquid, in this case water, needs to be exchanged with a new solvent having a low surface tension and allowing the hydrophobization agent to react with the silanol groups.

Extensive research have already been dedicated to this approach, which in the early protocols [14, 15] required several gel washings, solvent exchanges and high amounts of hydrophobization agent, resulting in a long and expensive process, hampering the synthesis on an industrial scale. Schwertfeger et al. [35] developed a synthesis route using ion exchanged water glass as precursor and reduced the amount of solvent exchanges to only one, which occurred simultaneously during the hydrophobization. Aged silica hydrogels were immersed in hexamethyldisiloxane (HMDSO) and trimethylchlorosilane (TMCS) was added to react with the silanol groups on the backbone and replace them by trimethylsilyl groups with release of hydrochloric acid (HCl). TMCS reacts also heavily with water to form HMDSO and the latter can react back to TMCS with HCl. This is shown in Eqs. (1) and (2) below:

$$\text{TMCS} + {\equiv}\text{Si} - \text{OH} \rightarrow {\equiv}\text{Si} - \text{O} - \text{Si(CH}_3)_3 + \text{HCl} \tag{1}$$

$$2\text{TMCS} + \text{H}_2\text{O} \rightleftharpoons \text{HMDSO} + 2\text{HCl} \tag{2}$$

The hydrophobic methyl groups help the pore water to go out. A phase separation of superhydrophobic organogel filled with HMDSO floating on a water phase containing acid and unreacted substances got formed. The wet gel could then be easily removed and dried at ambient conditions, without substantial shrinkage and thus aerogel was obtained. However, because high amounts of TMCS and HMDSO were required, Lee et al. [18] replaced the HMDSO with the cheaper Hexane and Isopropyl alcohol (IPA). IPA was added as a transition liquid as it has a polar and nonpolar part and therefore guarantees a more efficient exchange from water (polar) to hexane (nonpolar). After silylation the pores are also mainly filled with HMDSO rather than hexane, which surrounds the gel. This typical combined solvent exchange and hydrophobization [18, 40, 41] is however still very inefficient, especially on industrial scale, as a quantitative conversion of all free surface hydroxide groups of the wet gel can require a five to tenfold excess of the hydrophobization agent, making the use of an inexpensive water glass precursor pointless as the majority of the most expensive component in the synthesis, the hydrophobization agent, is wasted [4]. Another disadvantage is that high amounts of the very corrosive HCl from the TMCS got formed and part remains inside the aerogel.

The company JIOS Aerogel patented a co-precursor method [42, 43] in which hydrophobization and solvent exchange occur simultaneously during gelation, also using water glass as precursor, but without prior ion exchange, as most sodium ions get washed out during the solvent exchange. The procedure is almost identical to the one described by Bhagat et al. [19] and allows a fast (5 h) and cheaper production of aerogel powder. However, this co-precursor method is difficult to control and the gel does not get time to age and gain strength. Therefore, especially on industrial scale, a separate gelation and hydrophobization is preferred [4].

The aim of this work was then to obtain aerogel powder from water glass and dried at ambient pressure, with a thermal conductivity comparable to today's standards, but with a small standard deviation. Furthermore, the gelation had to occur without an ion exchange resin or high amounts of acid, while a combined solvent exchange and hydrophobization process was established using only minimal amounts of silylating agent and solvent.

2. Materials and methods

2.1. Silica aerogel powder synthesis

The protocol to synthesize silica aerogel powder is shown as a schematic representation in Fig. 1. Sodium silicate (water glass, 39–40% silicates in water with 7.80–8.50% Na_2O and 25.80–28.50% SiO_2) from abcr GmbH (Germany) was used as precursor, TMCS and HMDSO were obtained from Sigma-Aldrich. Hexane-(n) a.r., IPA and nitric acid (HNO_3, 65%) were ordered from Chem-Lab and HCl, 37% from Fisher Chemical. Water glass was diluted in beakers with distilled water until a silica content of 8 and 6 wt% were obtained, further referred as protocol 1 and protocol 2, respectively. Both sodium silicate solutions were stirred vigorously, but without formation of bubbles. A 3 M HCl solution was added to these mixtures using a syringe pump to ensure repeatability, while stirring slowly, until a pH of 10.85 and 10.55 was reached, for 8 (protocol 1) and 6 wt% SiO_2 sols (protocol 2), respectively, after which the beakers were sealed with paraffin film immediately. Gelation started for both samples and the solution turned light blue. After 30 min, a hard gel was obtained and put to age for 24 h at 22 °C, during which it turned opaque white. Each gel was then crushed and immersed in hexane in 5:3 volume ratio. IPA in an amount half of the hexane was then added as well as TMCS under low stirring (< 300 rpm). A silica:trimethylsilane(TMS) molar ratio of 1:4 was chosen. The reaction was first very exothermic and temperatures over 50 °C were reached, which dropped down after a few hours. A heater then maintained the temperature at 40 °C. During this process gel is hydrophobized and solvent exchanged at the same time. A clear phase separation could be observed after 5 h, the gel being filled with hexane and HMDSO, therefore called organogel [4], was floating on a yellow phase, which consisted mostly of the initial pore water, HCl from the TMCS, IPA, sodium ions. An aerogel powder was obtained by removing this yellow phase and drying the gel first at room temperature for 12 h and later in an oven at 150 °C for 3 h to evaporate the remaining

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