Functionalized aerogels – new nanomaterials for energy-efficient building. Preliminary AFM, Nanoidentation and EIS studies

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Abstract. Aerogels are highly porous nanostructured materials with excellent thermal insulation properties. The possibility to add additional function – to functionalize the aerogels, especially to produce photovoltaic electricity, will make them an excellent candidate for energy-efficient building. Going in the direction of this midterm goal we start with the investigation of the properties of the readily available silica aerogels. Atomic Force Microscopy reveals large areas with submicrometer roughness, which allows reliable nanoidentation measurements. The average hardness was measured to be 2.2 MPa and the Young’s modulus was 11 MPa, values typical for low density elastic silica aerogels. Electrochemical Impedance Spectroscopy, measured in ambient air, shows typical capacitive behaviour and the aerogel is best modelled by serially connected resistance of 37 kΩ and capacitor of 170 pF. The conductivity is interpreted in terms of proton migration, strongly dependant on air humidity.

1. Introduction
Aerogels are high surface area, highly porous nanostructured materials with the lowest bulk density of any known porous solid. It is derived from a gel in which the liquid component of the gel has been replaced with a gas. The result is an extremely low-density solid, with a notable effectiveness as a thermal insulator. Aerogels, which retain the free void volume of the wet gel, can be made from any material that can be processed as a gel. Outstanding properties include superior surface areas (from 100 to 1000 m²/g) and a bicontinuous pore–solid network in which the networked particles are 2–20 nm in diameter and covalently bonded together. The majority of pore volume in the mesoporous network resides in pores between 2 and 50 nm in size, the classical definition of mesoporosity. Aerogels are distinguished from the more commonly known xerogels by their relatively greater porosity, but more importantly by the continuity of the pore network throughout the solid, which
facilitates diffusive mass transport at near open-medium diffusion rates. The high surface area and fast diffusive mass-transport rates within aerogels have motivated investigations into their application as catalysts, battery materials, sensor materials and supports for fuel-cell catalysts. Expressing functional materials as aerogels has yielded improved performance over analogous materials made by other means, and in some cases has revealed new mechanistic components in complex interfacial processes. In this work we review the properties and study the most widely spread and commercially available aerogels - silica aerogels.

Silica aerogel is a translucent material consisting of a nanostructured SiO$_2$ network [1]. These are materials with unusual properties such as high specific surface area (500–1200 m$^2$/g), high porosity (80–99.8%), low density (~0.003 g/cm$^3$), high thermal insulation value (0.005 W/mK), ultra low dielectric constant ($k$ = 1.0–2.0) and low index of refraction (~1.05) [2, 3, 4, 5, 6]. In fact, silica aerogels hold 15 Guinness world records, among which for smallest density solid and for best thermal insulator. Earlier production of silica aerogels included supercritical drying and expensive raw materials like tetraethoxysilane. A new process was developed [7]. The silica hydrogels were prepared with water glass as a starting material. Silation is carried out in the water phase of the hydrogel which results in a reaction induced phase separation of gel water and solvent. Silica aerogel is a promising material for applications in building envelopes because of its high visual transmittance and its low thermal conductivity. Its thermal insulation properties are 2 times better then the mineral wool and 4 times better than Perlite. Besides its low thermal conductivity the aerogel is load bearing which makes it attractive for evacuated transparent insulation applications. Its impressive load bearing abilities are due to the dendritic microstructure, in which spherical particles of average size 2–5 nm are fused together into clusters. These clusters form a three-dimensional highly porous structure of almost fractal chains. The average size and density of the pores can be controlled during the manufacturing process.

The Parliament and Government of the European Union this year adopted a revised 2002 Directive on Energy Performance of Buildings, which requires that at the end of 2018 all new public buildings and by the end of 2020 all new buildings be of a type “nearly zero energy buildings”. This definition includes both energy consumption, which implies production of the energy from renewable sources within or near building, and greenhouse gas emissions. A multi-annual plan and a strategy for energy-efficient building was developed and adopted in final form several months ago [8]. In view of this plan our midterm goal is to add additional functionality to the excellent thermal insulation properties of the aerogels – to functionalize them. More specifically, we will pursue the possibility to add the functionality of photovoltaic electric current production in the aerogels. These, probably, will be aerogels from semiconductor quantum dots, which were recently synthesized [9]. First step towards this goal is to measure some physical properties of readily available aerogels. In this paper the results from the study of the surface morphology using Atomic Force Microscope (AFM), the mechanical properties with the help of Berkovich Nanoindenter, and electrical properties by the method of Electrochemical Impedance Spectroscopy (EIS) of silica aerogel are reported.

2. Experimental

Monolithic hydrophilic silica aerogel in the form of cylinders 7-8 mm in height and 22 mm in diameter were purchased from Aerogel Technologies, LLC (USA). The AFM used was model Q-Scope from Ambios Technology Corporation (USA) integrated with the Nanoindenter model APEX, manufactured by CETR (USA). The AFM was equipped with 80 µm scanner (95 µm available) and was used in dynamic mode with simultaneous measurement of topography and phase contrast. The movement back and forward from the AFM to the Berkovich diamond indentation tip with radius of 70 nm was automated. Both instruments were equipped with optical microscopes and image recording. EIS was measured in ambient air with a Frequency Response Analyzer from Advanced Technologies Ltd. (Bulgaria) working in the range 0.02 Hz – 32 MHz and capable of measuring samples with resistances up to 10$^{12}$ Ω. Al electrodes - 5 mm wide, were evaporated in vacuum on both sides of the
aerogel and visualized with the AFM. However, the reported here EIS data was measured with electrodes directly stuck in the aerogel and stabilized with silver paste.

3. Results and discussion
The surface of the aerogel, measured with the AFM is shown on figure 1. The roughness of the surface at some select points was below 100 nm – smooth enough for reliable nanoidentation measurements. The evaporation of Al electrodes on the aerogel produced higher but smoother features (figure 2). On scanning at larger areas one could see the grooves of the metal discs, in which the monoliths were cast. In the optical microscopy (figure 3) it is seen that the surface has some features on a submillimeter scale. Before performing the nanoidentation tests, optically smooth surface was chosen and visualized with the AFM.

Figure 1. AFM image of the surface of the aerogel.

Figure 2. AFM image of the surface of the Al electrodes vacuum evaporated on both sides of the aerogel.

Nanoindentation permits to probe the mechanics of nanomaterials and permits direct physical property measurements of heterogeneous materials with high spatial resolution [10]. The surface indents, as seen in the optical microscopes, are shown on figure 3. It should be noted that we have
done a large number of indents varying both the used force and the spacing but the results for the hardness and Young’s modulus were highly reproducible. One typical result is shown in figure 4. It should be pointed out that aerogels are not well characterized by hardness or the classical Oliver and Pharr theory, because homogeneous, isotropic materials are assumed here, as well as linear elasticity. Aerogels may be characterized by an extended Oliver and Pharr approach, which deals with porosity, non-linear elasticity, coatings, and we will try to access such software in the future. Nanindentation results are shown in figure 4. In the experiment shown we use a script for measuring at 3 points and in each point we have partial loading and unloading in ¼ steps from the maximal force of 55 mN. Hardness in the experiment shown varies from 0.9 to 4.5 MPa while the Young’s modulus was in the range from 2 to 20 MPa. Contact depth was in the 10 to 60 µm range. These results coincide with the data obtained for low density (0.08 – 0.5 g/cm$^3$) samples measured previously [11], which show elastic behaviour, while the denser aerogels behave as elasto-plastic materials.

**Figure 3.** A row of indents during the indentation process (left). The Berkovich indenter and its reflection are seen. On the right, 12 indents in a row, which partly overlap due to the large force used.

**Figure 4.** Nanindentation results. In this experiment at 3 different locations 4 partial loadings and unloadings were performed (left). On the right are the calculated values for the hardness and Young’s modulus for all 12 points. The most reliable measurement is the 1st one with filled symbols.

Results from the EIS measurements are shown on figure 5. The Nyquist plot is typical for pure capacitance behaviour. A modelling of the results was performed by fitting the raw data with a
predefined circuitry. The best fit was obtained by serially connected resistor with value of 37 kΩ and capacitor of 170 pF. Previously a strong dependence of the resistance on relative air humidity was reported [12] for silica aerogels with relatively high density. For humidities above 80% the resistance was in the subkΩ region, while for humidities below 58% it was in the MΩ region. These testify that the uptake of adsorbed water is a two-regime process. This mechanism of water adsorption was proposed by Dubinin and Serpinsky (D.S. theory) [13]. According to this theory, at lower relative humidity, the water forms a layer of clusters along the walls of the matrix of interconnected pores. At higher relative humidity, new water molecules start filling the remaining pore space through capillary condensation. The mobile species responsible for electrical conduction was traced out as protons and the proton conduction was highly augmented by the presence of adsorbed water. The proton migration seems to be greatly facilitated by the presence of water, suggesting that the mobility of ions is highly enhanced by the adsorbed water and the proton migration is primarily dominated by Grothuss mechanism. In this mechanism, the proton forms a H$_3$O$^+$ ion and jumps to the neighboring lone pair of electrons of a water molecule.

![Graph 1](image1.png)

![Graph 2](image2.png)

**Figure 5.** Results from the EIS measurements – Nyquist plot (left) and Bode plots.

4. Conclusion
Aerogels, especially if additional functionality like electricity production is added, are promising new nanomaterials in the area of energy-efficient building. Here we present preliminary studies of silica aerogels – the material that holds many records, for lowest density solid and best thermal insulator among them. We investigated in this paper the surface morphology with the help of Atomic Force Microscopy. Areas with submicron roughness are present and the evaporated Al electrodes show little increase in roughness. Mechanical properties were measured with Berkovich Nanoindenter. The average hardness was measured to be 2.2 MPa and the Young’s modulus was 11 MPa, values typical for low density elastic silica aerogels. Electrochemical Impedance Spectroscopy, measured in ambient air, shows typical capacitive behaviour and the aerogel is best modelled by serially connected resistance of 37 kΩ and capacitor of 170 pF. The conductivity is interpreted in terms of proton migration, strongly dependant on air humidity.

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