A New Type Preparation of Ultralight Elastic PAN/SiC Aerogels with High Thermal Stability

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Abstract. Owing to high porosity and thermal insulation, aerogels have attracted considerable academic and industrial interest in the applications of many industries in recent years. SiC aerogel and SiC aerogel-like structure which own both good properties of aerogel materials and high performance of SiC materials have a wide application prospect. In this paper, polyacrylonitrile (PAN) nanofibrous membrane was prepared by electrospinning, PAN/SiC aerogels were synthesized by introduction of SiC nanowhiskers by freeze-drying method and thermal modification. On the hand PAN nanofibers, as a respective of organic materials, have acid resistance and good flexibility. On the other hand SiC nanowhiskers play a supporting role, and can keep structure stability. The results show that PAN/SiC aerogels with new procedure holds good integrated performances.

1. Introduction

Highly porous aerogels, as a respective of three-dimensional (3D) versatile nanomaterials, have attracted considerable attention. The multiple functional properties of aerogels, such as high porosity, high surface area, low density, and ultra-light weight, make these materials promising for a wide range of applications including thermal insulations [1], supercapacitors [2-3], sensors [4], water desalination [5], catalysts [6] and others.

Meanwhile, SiC possesses so many excellent performances such as high thermal stability, oxidation resistance, chemical inertness, low coefficient of thermal expansion, good abrasive resistance and mechanical strength. [7-8] these properties make it attractive in various applications especially in harsh environments, for example, catalyst support, gas-burner media and high-temperature filtering (molten-metal/diesel-particulates). [9] Because of the remarkable potential of SiC, many research groups have explored a variety of approaches to make use of SiC materials. Up to now, a few papers have been reported the SiC aerogels (or SiC aerogels-like) are fabricated with different methods and applied in many fields. For instance, CHEN Ke et al. [10] synthesized Silicon Carbide aerogel with Templated-Confined Magnesiothermic Reaction in which there are many complicated processes including carbonization reaction, magnesium thermal reaction and other procedures during which special atmosphere and temperature conditions were needed strictly. XU Zi-jie et al. [11] prepared aerogel-like C/SiC by sol-gel and carbothermal progress which were heated in argon atmosphere at 1800°C. As we all know, porous SiC aerogels is usually prepared through carbothermal reduction which needs extremely high temperature, and the preparation process is usually elaborate which contains various
chemical reactions. [12-13] Therefore it is necessary to develop a new method to prepare SiC aerogel or SiC aerogel-like materials.

In this paper, a novel and simple method has been developed to synthesis composite polyacrylonitrile/silicon carbide (PAN/SiC) aerogels (or SiC aerogel-like) with improved thermal-resistance using an inexpensive organic-inorganic precursor system via freeze-drying method. Structural characteristics of PAN/SiC aerogels (or SiC aerogel-like) retained during heat treatment. Moreover, prepared samples presented high thermal properties and mechanical property, due to the presence of partially SiC nanoparticles in the structure of fabricated aerogels.

2. Experimental

2.1. Preparation of nanofiber membranes

The polymeric precursor solution consists of N, N-dimethylformamide (DMF, AR, Tianjin Fuyu Fine Chemical Co. Ltd.), and polyacrylonitrile (PAN, M_\text{w} \sim 500,000), the mass ratio is 22:3. The prepared solution should be stirred by magnetic stirrer (HJ-4A, JinTan Youyi Instrument Institute) thoroughly for 24 h. Then precursor solution was injected into a 10 ml plastic syringe with a flattened stainless steel needle (with an inner diameter of 0.72 mm and an outer diameter of 1.08 mm). The HVPS (high voltage power, DW-P303-1ACFO, TianJin Dongwen High Voltage), syringe pump (LSP01-1A, Baoding Longerpump), injection syringe was connected to compose spinning device. The applied high voltage was 18 kV, the distance between the syringe needle and the roller collector was 15 cm, and the feeding rate of solution was 35 \mu l/min. All the experiments were carried out at room temperature to gain PAN nanofibers which have good acid resistance and other properties.

2.2. Fabrication of aerogels

75 wt% PAN nanofiber membrane and 25 wt% SiC nanowhiskers were put in deionized water/tert-butanol mixture (mass ratio of 4:1). The weight ratio of solid dispersion and total dispersion (liquid and solid) was 1:100. Then the mixture was homogenized for 30 min at 10,000 rpm by homogenizer to make sure that the nanofiber membrane and SiC was dispersed equably. Next the dispersion was poured into the desired mould, quick-frozen in liquid nitrogen, annealed at -10\degree C for 8 h, then the PAN/SiC frozen aerogels were transferred into a freeze-dryer (FD-1-50, China) under vacuum lower than 30 Pa for two days. At last the as-prepared aerogels were heated at 300\degree C for 2 h at a heating rate of 3 \degree C min^{-1} by hot blast drying oven to obtain aerogels with better morphology.

2.3. Sample characterization

Bulk densities were calculated from the weight and the physical dimensions of the samples. Surface appearance could be watched by eyes directly, and inner structures were measured by a scanning electron microscope (SEM, TM-1000, Hitachi). Nitrogenadsorption measurements were run on an accelerated surface area and porosimetry system (3H-2000PS2 unit, BeishideInstrument S&T Co. Ltd.). The thermal stability was detected by thermogravimetric analysis (TGA, Mettler-ToledoTGA/DSC). And the apparent morphology and microstructure of aerogels via heat treatment are contrasted at different temperature. The phases were identified by X-ray diffraction (XRD) (X’pert PRO MPD, Philips, Netherlands) in the angular 10-90\degree with the scan speed of 2 \degree /min. The chemical compositions were analyzed by Fourier transform infrared spectroscopy (FTIR) using a Thermo Scientific Nicolet iN10 spectrometer and transmittance data were processed for the wave number range 500-4000 cm^{-1}.

3. Results and discussion

The composite aerogels were fabricated by electrospinning, freeze drying and heating modified method. Fig. 1a1-a3 shows the photograph of untreated PAN/SiC composite aerogels, the as-prepared samples preserved monolithic morphology, but it has low elasticity due to that there is no crosslinking in adjacent fibers, which was attempted to improve via heat modification. Aerogels shown in Fig. 1b1-b3 were obtained from original aerogels by heating at 300 \degree C for 2 h at a heating rate of 3 \degree C min^{-1} by hot blast drying.
drying oven. The temperature of 300 °C cannot exert an effect on SiC, but can cause an obvious change of PAN nanofibers, because heating at 180 °C-300 °C under air atmosphere is an essential low-temperature thermal stabilization step. Under this heating procedure at 180 °C-300 °C, cyclization reaction occurs on the molecular chains of PAN fibers, which results in the stabilization of PAN fiber and gives rise to a thermally stable cyclized structure. [14-15] meanwhile, a certain degree of structural transformation of PAN nanofibers basic structure takes place, the aerogel material shrinks and has a certain degree of elasticity.

![Figure 1](image1.png)

**Figure 1.** Photograph of aerogels: shape stability of original aerogels (PAN/SiC aerogels) (a1) before, (a2) under and (a3) after compression by 100 g weight; Shape stability of modified PAN/SiC aerogels (aerogels after 300°C heat treatment at air atmosphere) (b1) before, (b2) under and (b3) after compression by 100 g weight.

Figure 2 shows the SEM images of PAN/SiC composite aerogels, the thin consecutive fibers are PAN nanofibers and the thick intermittent fibers are silicon carbide whiskers. The diameter of PAN nanofibers is 50-150 nm, and the diameter of carbide whiskers are 200-500 nm (Fig. 2a). The major of the aerogels (75 wt %) are PAN nanofibers but they are soft. SiC whiskers account for a fraction of composite aerogels (25 wt %) and they play a supporting role. Some PAN nanofibers transformed to the stable cyclized structure and intertwined with each other after high temperature process, and the cyclized strcture plays a role as cross-linking agent in the junction point between adjacent PAN and/or fibers/whiskers (Fig. 2b, e.g., PAN nanofibers and PAN nanofibers, PAN nanofibers and SiC whiskers, SiC whiskers and SiC whiskers), so that the network structure of aerogels becomes more stronger.

![Figure 2](image2.png)

**Figure 2.** SEM images of: (a) original aerogel, (b) thermal modified PAN/SiC aerogel (aerogel after heat treatment at 300°C). The red circles in (b) show the melted PAN which acts as cross-linking agent in the nodes of adjacent fibers (whiskers).

Figure 3 shows the FTIR spectra of PAN powder and PAN/SiC aerogels. The FTIR spectra of the PAN powder exhibited that the band at 1736 cm\(^{-1}\) is assigned to the carbonyl group (C=O), the band at 2245 is assigned to the nitrile groups (C≡N), the bands at 1455 cm\(^{-1}\) and 2490 cm\(^{-1}\) are ascribed to C-H. [16-17] obviously, those chemical bonds still existed in the thermal modified PAN/SiC aerogels after heat treatment at 300°C. The slight decrease of the intensity about these bands of PAN appeared due to
the existence of SiC whiskers in aerogels. And the SiC-C bonds at 798 cm$^{-1}$ and 926 cm$^{-1}$[18-19] were observed.

Figure 4 shows the XRD patterns of the raw material and obtained product. All reflection peaks of be cubic SiC (card No.01-073-1665) [19-20] can be found in the heat modified PAN/SiC the aerogels, and the SiC can keep stability at high temperature. The peak at $2\theta$ values of 16-17° is related to PAN, [21] it can be observed at the XRD pattern of heat modified PAN/SiC aerogels, indicating that the PAN nanofibers and SiC whisker existed in composited aerogels.

Figure 5 shows the nitrogen adsorption/desorption isotherms and the pore-size distribution of the PAN/SiC aerogels. The BET specific surface area is 31.53 m$^2$g$^{-1}$, the pore volume is 0.04152 cm$^3$g$^{-1}$ and pore size is smaller than 112.5 nm. The major pores can not be measured by BET methods, because a large proportion of pores of PAN/SiC composite aerogels are larger than 1 μm (Fig. 2) and only pores smaller than 200 nm can be tested by BET method. The specific surface area, pore volume and pore diameter are far beyond numbers mentioned before. So calculated porosity by calculation through formula $p = (1 - \rho_b/\rho_s) \times 100\%$, $\rho_b$ is the bulk density, and $\rho_s$ is skeletal density. $\rho_b$ can be contained by calculation from volume and weight. There are 25 wt% SiC nano whiskers and 75 wt% PAN nanofibers in the sample, so $\rho_s = 25\% \times \rho_{SiC} + 75\% \times \rho_{PAN}$, $\rho_{SiC} = 2.7$ g/cm$^3$, $\rho_{PAN} = 0.797$ g/cm$^3$, The porosity of aerogels was 99.24%.

Figure 6 shows the TG curve of the PAN/SiC composite aerogels. It is obvious that although there are some weight loss in some extent in a range of 300 °C to 500 °C, almost no weight loss bellow 300 °C and above 500 °C. The weight loss in 300 °C to 500 °C was due to the pyrolysis of PAN nanofibers.
4. Conclusion
In summary, a novel and simple method has been demonstrated to fabricate PAN/SiC aerogels (or SiC aerogel-like) via freeze-drying and electrospinning method. The as-prepared PAN/SiC aerogels showing some extent elastic property. The aerogels own high porosity which is 99.24 % through rough calculation. With some extent of mass loss and volume shrinkage during thermal modified process and the porous structure can be maintained. The PAN/SiC aerogels have good heat resistance as well as hardly no mass loss under the heat treatment lower than 300℃, which could be used as reaction supports in some acid resistance environments.

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