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Fabrication of pre-oxidation polyacronitrile (PAN) hollow microspheres

Shixiang Dong[a,b], Wei Han[a], Meifang Liu[b], Zhangwen Zhang[b], Bo Li[b,*], Liqin Ge[a,*]

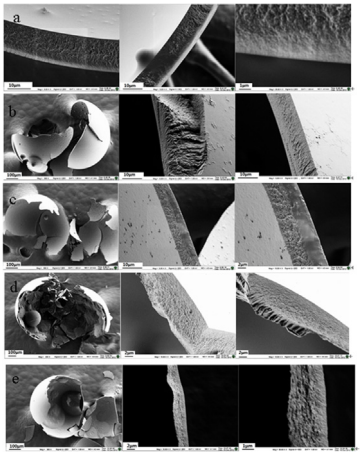
[a] State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, PR China
[b] Laser Fusion Research Center, China Academy of Engineering Physics, Mianyang 621900, PR China

HIGHLIGHTS

- Three various double emulsions (O1/W/O2) made by the double emulsion stirring method.
- Solvent – free PAN hollow microspheres made by the supercritical drying process.
- The skin-core structure of Pre-oxidation microspheres is associated with pre-oxidation conditions.
- Pre-oxidation microspheres' have remarkable advantages of pressure-resistance comparing to the plastic ones.
- Pre-oxidation PAN microspheres at 300 °C have best mechanical performance than the others.

GRAPHICAL ABSTRACT

The FESEM images of the wall section of PAN pre-oxidation microspheres under different temperatures:260 °C (a), 280 °C (b), 300 °C (c), 320 °C (d), 340 °C (e).



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ABSTRACT

The control PAN plastic microspheres were obtained after the evaporation of the middle solvent from silicon oil/PAN in DMF solution/silicon double emulsions (O1/W/O2) which were prepared with stirring method. The pre-oxidation PAN microspheres were prepared after the heating treatment of the PAN plastic microspheres successfully. The structures of the PAN pre-oxidation microspheres were characterized by the Stereomicroscope, the Field Emission Scanning Electron Microscope (FESEM), and the Fourier Transform Infrared spectroscopy (FTIR). It was found that the pre-oxidation PAN microspheres have best mechanical performance than the others at 300 °C. The pre-oxidation microspheres' pressure-resistance results showed that they can bear greater pressure than the plastic ones, which means that the microspheres' mechanical strength has been enhanced after the heating treatment. Most pre-oxidation microspheres can bear the pressure higher than 17 MPa, which provide a great prospect in the target application.

1. Introduction

With the ongoing development of human society, energy issues have become increasingly prominent [1,2]. Traditional fossil fuels

* Corresponding authors.
E-mail addresses: lb6711@126.com (B. Li), lqge@seu.edu.cn (L. Ge).

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are non-renewable sources of energy that lead to a variety of serious environmental problems with long-term use. The dual challenge of environmental problems and future energy shortages aregradually becoming hindrances to further development [3]. To address these issues from a traditional vantage point, clean and efficient sources of energy have beenutilized, including wind, solar, and nuclear energy. Of these new energy sources, nuclear energy has been most widely researched currently for its potential applications.

Nuclear fusion and nuclear fission are the two methods to generate nuclear energy. However, nuclear fission can produce a large number of gamma rays, and materials and byproducts contain a high level of radioactive isotopes of heavy metals [4,5]. If handled improperly, these materials and waste products would have a very serious adverse impact on the environment and human. Given this circumstance, nuclear fusion is currently the energy-providing method of choice for those interested in nuclear energy.

The ICF (Inertial Confinement Fusion) experiment has recently drawn greater attentions for researchers [6–8]. In this experiment, a key step was to fabricate desirable targets [9]. As a fuel container, targets must satisfy the geometric parameter requirements and have specific physical and chemical properties [10,11]. Polymer targets have the advantages of low density, permeability and atomic number, and good resistance to radiation corrosion [12]. Compared with traditional polystyrene (PS) and polymer vinyl acetate (PVA) targets, polyacrylonitrile (PAN) targets possess higher mechanical strength and lower deuterium–tritium permeability (shown in Table 1) [13–15]. PAN, an important precursor of polymer materials, is known for its chemical stability and strong anti-corrosion and anti-radiation properties, characteristics that effectively prevent the penetration of gas [16–19]. PAN contains a strong —CN structure that is similar in effect to that of hydrogen bonds [20]. The strong interaction between the molecular chains, arising from —CN bond make the hydrogen-barrier properties improved Accordingly, PAN is a potential material for the fabrication of ICF targets.

PAN (which attains its mechanical strength and chemical stability through heat treatment) is widely used for carbon fibers [21]. The process of converting PAN fibers into PAN carbon fibers mainly includes molding, pre-oxidation, and a carbonization which was also investigated in early researches [22,23]. The PAN-based pyrolysis reaction combines prestabilization and carbonization and contains intrachain cyclization, dehydration and denitrogenation [24,25]. The whole chemical reaction can convert a linear polymer into turbostratic carbon by increasing the heating temperature [26,27].

In this paper, we characterize and detect the microstructures and properties of pre-oxidation PAN microspheres at different treatment temperatures. Additionally, we hope to prepare the hollow PAN microspheres with higher intensity and better performance with respect to gas retention so that suitable polymer or carbon targets are developed for use in the fusion process.

2. Experimental section

2.1. Materials

PAN powders (Mw: 60000) and *N*, *N*-dimethylformamide (DMF) were obtained from Sigma-Aldrich CO. Ltd and Sinopharm Chemical Reagent Co. Ltd. Aliquat°336 was bought from Alfa Aesar A Johnson Matthey Company, England. The KF-96-1cst/KF-96-5cst/KF-96-10cst/KF-96-50cst silicon oils were obtained from Shin-Etsu Chemical Co. Ltd. Japan. The PAN powders were dissolved in DMF (1:6.67 (w/v)) homogeneously. All the chemicals were used as received without any purification.

Table 1
Comparisons the property of PAN materials with other materials.

	PS	PAN	PVA
The gas permeability coefficient of the deuterium gas/mo m^{-1} s^{-1} Pa^{-1}	$\sim 10^{-14}$	$\sim 10^{-17}$	$10^{-18} \sim 10^{-20}$
Tensile strength/MPa	80	»600	60–100
Low temperature resistance	bad	well	bad
Irradiation resistance	well	well	bad

2.2. Preparation of PAN solution

4.5 g PAN powders were dissolved in 30 ml DMF with 3 ml Aliquat°336 to form 15% PAN (m/v) solution.

2.3. Preparation of PAN microspheres using the double emulsion stirring method

To obtain PAN hollow microspheres, one should prepare the double emulsions, the oil/PAN solution/oil (O1/W/O2) system. The first step is that silicone oil is dropped into PAN solution during stirring (Vo_1:V_{PAN}. is 1:2–1.5:2).

The second step is that single emulsion droplets which obtained in the first step were added in the bulk with same viscosity of silicone oil (Vo_1/w: Vo_2 is 1:100) and stirring constantly. Thereafter, the mixed solution was kept stirring 24 h at room temperature in order to volatilize DMF organic solvents, promoting PAN hollow microspheres solidification (Fig. 1).

2.4. Preparation of solvent-free hollow PAN microspheres

Three different drying methods were studied in order to remove the silicon oil in the PAN microspheres: *n*-hexane wash, nature volatile and supercritical drying. Compared to the others, the CO_2 supercritical drying method is subject to keep the PAN capsules integrality. CO_2 supercritical drying process consists of two steps,the first, solvent exchange, where the PAN capsules were immerged in sequence silicone oil with different low viscosity with 30cst, 10cst, 5cst, 1cst, 0.65cst.Finally, immerged in the isoamyl acetate to remove silicone oil.The second, supercritical drying, substituted the isoamyl acetate for liquid carbon dioxide and carbon dioxide evaporated in supercritical environment. The non-solvent hollow PAN microspheres were obtained.

2.5. Heat treatments of solvent-free PAN microspheres

Solvent-free PAN microspheres were oxidated at 260 °C, 280 °C, 300 °C, 320 °C, 340 °C respectively with a heating rate of 3 °C/min, and kept at 260 °C, 280 °C, 300 °C, 320 °C, 340 °C for 2 h in air. Then the pre-oxidation microspheres were carbonized at 800 °C with a heating rate of 16 °C/min, and kept for 3 min under the protection of high purity Argon (Ar).

2.6. Characterizations of PAN microspheres

Photographs of the microspheres were taken by the optical stereo scopic microscope (Olympus U-LH75XEAPO, Tokyo, Japan) equipped with the charge couple-device camera (Evolution MP 5.0 and DP72, Olympus Corporation) based on different amplification factors. The morphology images of the microspheres were taken with the Zeiss Ultra Plus field emission SEM operating at 2–7 kV (Zeiss, Oberkochen, Germany). The elemental analysis was conducted by the energy dispersive X-ray analysis (EDS) linked to the FESEM.