

# Preparation of Mesophase Pitch-Based Carbon Foams with Supercritical Toluene

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Received 29 January 2010; accepted 10 October 2010

DOI 10.1002/app.33607

Published online 18 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Mesophase pitch-based carbon foams were prepared with supercritical toluene. The effects of the foaming conditions, such as the solvent proportions, temperatures, initial pressures, and pressure drop rates, on the cell densities and mean cell diameters of the carbon foams were studied. The foaming mechanism was analyzed with the theories of homogeneous nucleation. The carbon foams varied in cell densities and cell structure from three-dimensional interconnected to closed sizing in the range 200 to 800  $\mu\text{m}$  when they were generated under

different conditions. The carbon foam structure could be optimized with cell densities of  $10\text{--}16 \times 10^3 \text{ cm}^{-3}$  and cell diameters from 400 to 450  $\mu\text{m}$ , under the conditions where the temperature was 588 K, the initial pressure was 3.0 MPa, the pressure drop rate was 1.5 MPa/s, and the solvent proportion was 30 wt %. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 336–341, 2011

**Key words:** blowing agents; inorganic materials; nucleation

## INTRODUCTION

In recent years, much attention has been focused on thermally conductive carbon foams. Hager et al.<sup>1</sup> predicted the existence of a new kind of carbon foam with a ligament–mesh structure at the 21st international carbon conference. In 1998, Klett et al.<sup>2</sup> discovered a porous graphite material accidentally when preparing carbon materials from pitch. The porous graphite showed a very high thermal conductivity. From then on, great interest has been aroused in this kind of carbon material, later called *carbon foam*.<sup>3–5</sup>

The performance of carbon foams, such as in their mechanical properties and thermal conductivity, is determined by not only the raw materials but also the foaming processes. High-pressure nitriding was an early process by which nitrogen was first forced to penetrate into a pitch powder and then discharged from the melt. Another process involved the addition of a solid foaming agent into a pitch to generate blowing gas above the melting point. The method used by Oakridge Laboratory was called *self-foaming*, by which a pitch was heated above its pyrolysis temperature while it became viscoelastic

and was blown into a foam. Each method involved a phase separation induced by temperature quenching, pressure quenching, or chemical pyrolysis. Beechem et al.<sup>6</sup> set up a numerical model to describe a single nonspherical bubble growth mechanism in a precursor. Rosebrock et al.<sup>7</sup> tried to simulate the growth and motion of graphite foam bubbles. Goel and Beckman<sup>8</sup> found that micropores in polymers could be thoroughly controlled by pressure drop with supercritical  $\text{CO}_2$  as a blowing agent and simulated homogeneous nucleation. Inspired by that, we previously brought forth a new approach by which pitch-based carbon foams with uniform cell sizes and highly opened pore ratios were prepared with supercritical toluene.<sup>9</sup> Later, Li et al.<sup>10</sup> gave a similar report.

In this study, the effects of the temperature, pressure, and pressure drop rate on the foam structure on the average bubble size and porosity were analyzed by nucleation simulation and experimental data.

## THEORY

### Thermodynamic analysis of the supercritical fluid (SCF)–pitch system

During the foaming process, pitch transforms from a viscous liquid to a solid because of a thermodynamic change in the system. The SCF–pitch system is approximate to an SCF–polymer system, which can be analyzed as a high-pressure liquid binary system. A binary system has three independent variables at

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50572015.

most. In this system, the thermodynamic criterion for intersolubility was  $\Delta G_m < 0$  and  $(\partial^2 \Delta G_m / \partial \phi_2^2)_{T,P} > 0$ , where  $\Delta G_m$  is the mixed Gibbs free energy,  $\phi_2$  is the volume percentage of the pitch,  $T$  is the absolute temperature, and  $P$  is the system pressure.  $\Delta G_m < 0$  is a necessary but insufficient condition for complete intersolubility.<sup>11</sup>

In this study, the SCF–pitch system belonged to a partially soluble system, for which  $\Delta G_m$  was less than zero. The system contained two equilibrium phases, a poor-pitch phase and a rich-pitch phase. When the pitch content lies between the two equilibrium phases, the system is unstable and tends to phase-separate at  $(\partial^2 \Delta G_m / \partial \phi_2^2)_{T,P} < 0$ . Therefore, changes in either the temperature or time could lead to phase separation, that is, bubble nucleation.

### Homogeneous nucleation theory

The rate of homogeneous nucleation can be described by the following equation:<sup>8</sup>

$$N_{\text{homo}} = f \frac{P}{H} \exp\left(-\frac{\Delta G_{\text{homo}}^*}{kT}\right) \quad (1)$$

where  $N_{\text{homo}}$  is the number of nuclei at critical radius ( $r_c$ ) generated per cubic centimeter per second;  $H$  is the Henry's coefficient;  $P/H$  is the concentration of the blowing agent in the polymer, that is, toluene in pitch for this study ( $\text{mol}/\text{cm}^3$ );  $k$  is Boltzmann's constant ( $k = 1.38 \times 10^{-23} \text{ J/K}$ ), and  $f$  is the frequency factor of the blowing agent. The term  $\Delta G_{\text{homo}}^*$  is the maximum Gibbs free energy for homogeneous nucleation and is given by

$$\Delta G_{\text{homo}}^* = \frac{16\pi\gamma^3}{3\Delta P^2} \quad (2)$$

$r_c$  of the nuclei is given by

$$r_c = \frac{2\gamma}{\Delta P} \quad (3)$$

where  $\Delta P$  is the magnitude of the quench pressure and  $\gamma$  is the surface energy of the bubble interface. Therefore, the total number of generated nuclei should be integrated across the procedure during which the gas pressure falls from the saturation pressure to the vitrifying pressure:

$$\begin{aligned} N_{\text{total}} &= \int_0^t N_{\text{homo}} dt = \int_0^t f \frac{P}{H} \exp\left(-\frac{\Delta G_{\text{homo}}^*}{kT}\right) dt \\ &= \int_P^0 f \frac{P}{H} \exp\left(-\frac{\Delta G_{\text{homo}}^*}{kT}\right) \frac{1}{dP/dt} dP \quad (4) \end{aligned}$$

where,  $t$  is foaming time.

## EXPERIMENTAL

### Materials

The mesophase pitch used was a product (labeled AR, Aromatic Resin) of Mitsubishi Chemical Co., Ltd. (Tokyo, Japan), with a softening point of  $558 \pm 5 \text{ K}$  and a mesophase content of 100 wt %.

The viscosity measurement was carried out on a rotational rheometer type ARES–RFS (New Castle, Deaware). The pitch powder was molded into a tablet with diameter of 20 mm and a thickness of 2 mm. The tablet was then placed on a hot stage of the rotational rheometer, pressed by a rotary upper flat rotating at 1 rad/s, and heated at 3 K/min to 603 K. The viscosity data were obtained by the stress and strain.

### Preparation method of the foams

Foaming was carried out in a 500-mL high-pressure vessel, into which a certain amount of the pitch (usually about 10 g) was added, along with a certain mass percents of the pitch's weight toluene taken by a measuring cylinder in a liquid state. The vessel was alternately vacuum-pumped and filled with nitrogen several times, set to a certain pressure, then heated to a certain temperature, and kept there for 3 h; when the pitch was saturated enough by the toluene, the SCF–pitch system reached phase equilibrium. Then, the pressure of the system was discharged at a certain rate. A pitch foam block about 60 mm round and 100 mm high were derived when the vessel was cooled.

The pitch foam blocks were oxidized in an aired oven at 523 K for 5 h, and then, the stabilized pitch foams were carbonized in a tube furnace (Shanghai, China) protected with nitrogen at 1273 K for 15 min.

### Characterization

The microstructure of the carbon foams was inspected under a JSM-5600LV scanning electric microscope (Tokyo, Japan). We prepared the samples by fracturing the carbon foams into small pieces, planishing carefully, and rinsing them in acetone with supersonic waves. The foams located in the upper, middle, and bottom of the reactor looked a little different. The images shown later were the middle ones, whereas the cell density and mean diameter for each were calculated by the three images. The cell number per cubic centimeter of a foam ( $N_{\text{total}}$ ) were calculated by the following equation, which was adopted by Kumar and Suh.<sup>12</sup>

$$N_{\text{total}} = (nM^2/A)^{3/2} \quad (5)$$

where  $A$  is the area of a scanning electron microscopy (SEM) picture of a carbon foam ( $\text{cm}^2$ ),  $n$  is the number

**TABLE I**  
**Demonstration of the Average Cell Diameter Obtained for the Carbon Foam Samples<sup>a</sup>**

	Upper	Middle	Bottom
Diameter data (m <sup>-6</sup> )	460, 396, 459, 421, 459, 452, 424, 465, 445, 431, 395, 422, 446, 463, 390, 419, 440, 389, 459, 379, 406, 407, 408, 390, 441, 410, 417, 384, 388, 439, 376, 427, 388, 435, 417, 377, 419, 394, 380, 401, 398, 400, 403, 407, 399, 403, 447, 420, 442, 405, 407, 442, 419	411, 370, 417, 413, 403, 380, 387, 366, 422, 437, 420, 400, 366, 373, 374, 413, 382, 371, 397, 435, 389, 419, 376, 376, 360, 414, 433, 384, 402, 403, 372, 403, 406, 405, 418, 435, 424, 412, 411, 377, 395, 410, 412, 373, 423, 393, 408, 431, 406, 435, 364, 421, 394, 427, 389, 370, 388, 372, 436, 423	395, 401, 361, 361, 383, 358, 412, 377, 363, 413, 400, 353, 381, 394, 399, 348, 407, 383, 402, 398, 348, 406, 408, 405, 415, 358, 351, 369, 405, 380, 348, 374, 348, 388, 354, 373, 389, 346, 358, 345, 403, 364, 364, 388, 391, 400, 356, 350, 357, 399, 410, 391, 355, 395, 377, 401, 375, 368, 372, 349, 373, 391, 363, 378, 383, 387
Average (m <sup>-6</sup> )	417 ± 45	401 ± 43	379 ± 34
Total average (m <sup>-6</sup> )		399 ± 41	

<sup>a</sup> Foaming conditions: 30 wt % toluene, 3.0 MPa, 588 K, and 1.5 MPa/s.

of cells on the picture, and  $M$  is the magnification. We calculated the mean cell diameter and error range for each sample by measuring all of the diameters of the cells on the pictures and dividing the sum with the total cell number, as demonstrated in Table I, which shows that the cell diameters were larger and distributed more widely for the upper parts.

## RESULTS AND DISCUSSION

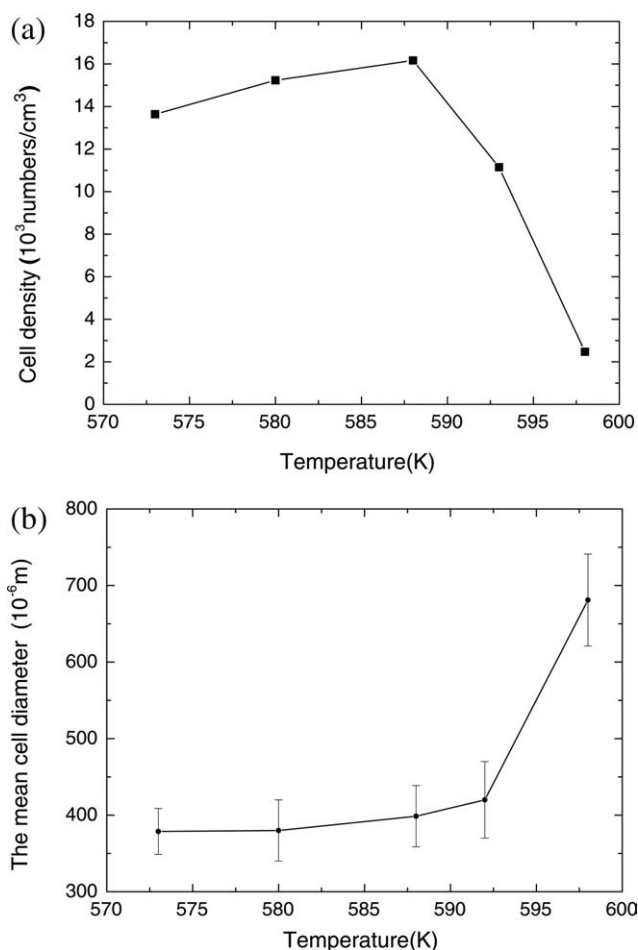
Pitch is partially soluble in many solvents, such as acetone, tetrahydrofuran, benzene, toluene, and pyridine, and is even completely soluble in quinoline. Toluene was chosen as the SCF based on the following two principles. First, it can be dissolved into molten pitch completely to form one phase compound and separated conditionally; second, the molten pitch must be kept in a viscoelastic state in the presence of the solvent. However, the bubble seeding and growing rates varied apparently with the initial nitrogen pressure, temperature, and pressure drop rate; this resulted in different structured foams.

### Effect of the temperature

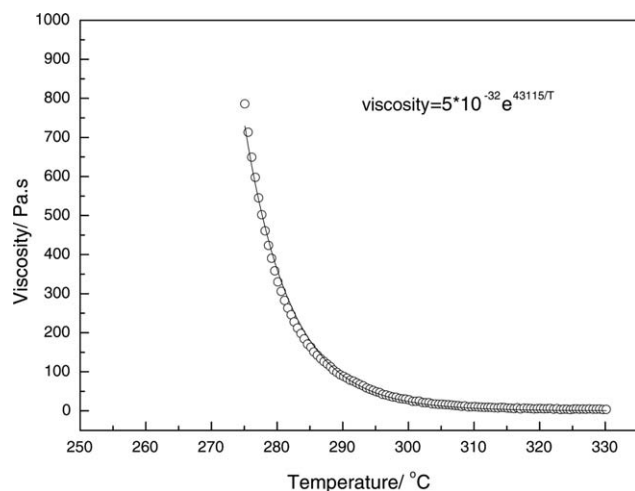
We studied the effect of the temperature on the final porous structure of the carbon foams in the range 573–598 K by fixing the initial pressure at 3.0 MPa, the proportion at 30 wt %, and the pressure drop rate at 1.5 MPa/s. As shown in Figure 1, the cell density of the carbon foams increased slowly at first and then declined rapidly after 588 K, whereas the mean cell diameter increased continuously, and the diameter distribution range increased as the temperature increased.

The mechanism of the foaming temperature influencing the final foam structures was complicated. According to eq. (4), when the temperature increases, the exponential part will be higher; however,  $H$  will be higher too. Therefore, it was reason-

able that there existed a maximum value for the nuclei number. Moreover, the cells were allowed to grow for a longer time because the interval between the melting and vitrifying temperatures was widened. The low viscosity also made it easy for the generated cells to coalesce; this resulted in large-size



**Figure 1** Effect of the temperature on the cell density and cell diameter.

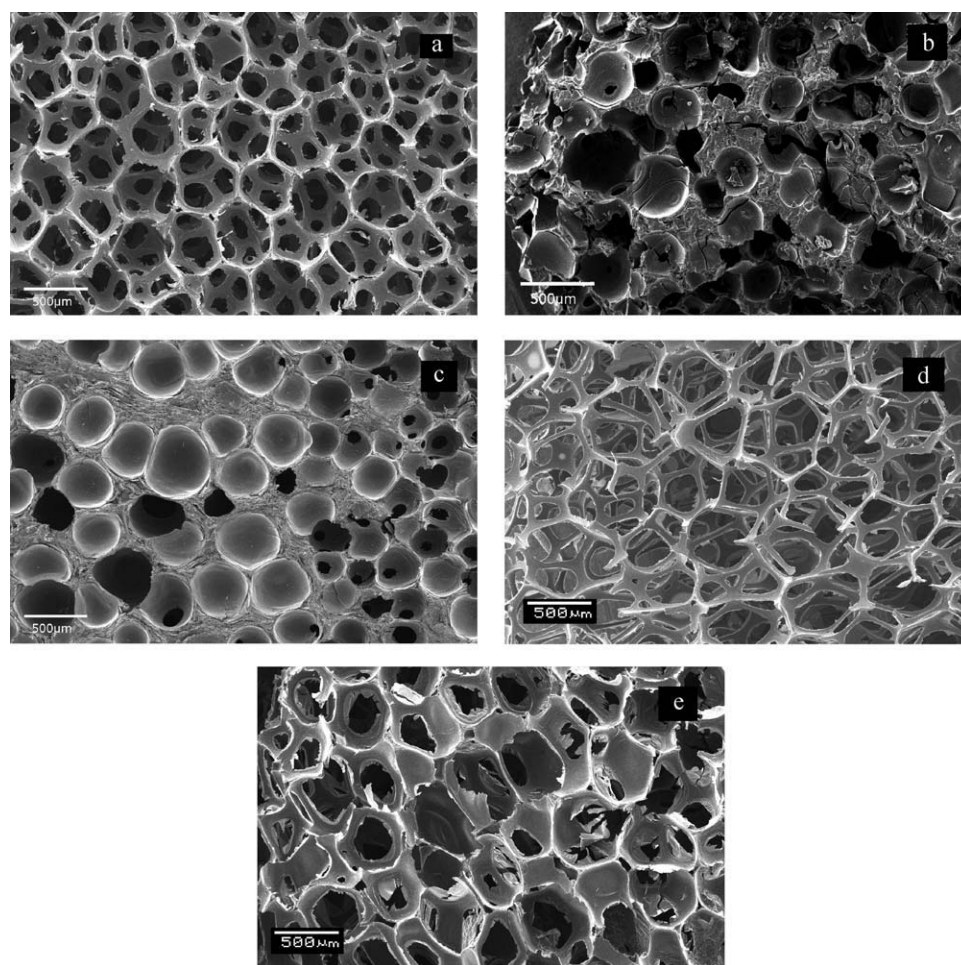


**Figure 2** Temperature dependence of the mesophase pitch viscosity.

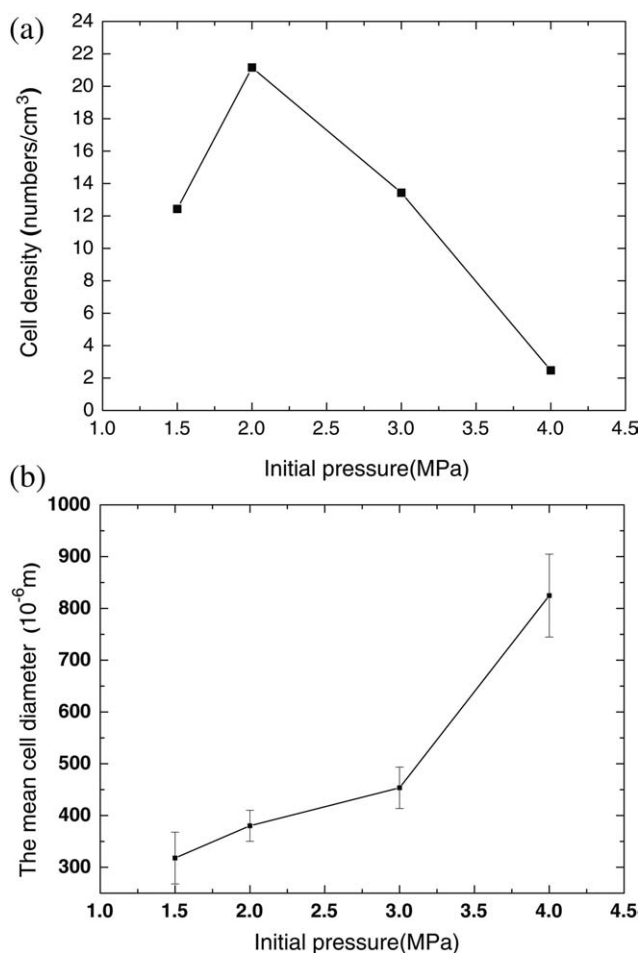
cells and a low cell density. Figure 2 describes the temperature dependence of the viscosity of the pitch. The pitch was very sensitive to the change in tem-

perature as a liquid crystal material and obeyed the Arrhenius equation. With increasing temperature, the viscosity dropped sharply, from 780 Pa s at 558 K to 162 Pa s at 568 K, into a viscoelastic state at which it could be easily formed into fibers and foams. Because the viscosity depended so much on the temperature, slight changes in the temperature resulted in a big difference in the derived foams.

Figure 3 shows the SEM structures of the derived carbon foams under different conditions. When the added toluene was 30 wt % of the pitch's weight, the initial pressure was set to 3.0 MPa, the temperature was 588 K, and the pressure drop rate was 1.5 MPa/s, many nuclei were generated, and they grew into each other to form three-dimensional networks, where the cell walls were stretched into ligaments with high orientation, as shown by Figure 2(a). Although the other conditions were fixed, except that the temperature was set at 573 K, as Figure 3(b) shows, fewer bubbles were generated and they were isolated from each other because of too fewer nuclei and insufficient growth.



**Figure 3** SEM photographs of the carbon foams derived under different foaming conditions: (a) 3.0 MPa, 588 K, 30 wt %, and 1.5 MPa/s; (b) 1.5 MPa, 573 K, 30 wt %, and 1.5 MPa/s; (c) 1.5 MPa, 588 K, 30 wt %, and 1.5 MPa/s; (d) 1.5 MPa, 588 K, 30 wt %, and 1.0 MPa/s; and (e) 1.5 MPa, 588 K, 10 wt %, and 1.5 MPa/s.



**Figure 4** Effect of the initial pressure on the cell density and cell diameter.

#### Effect of the initial pressure

We studied the effect of the initial pressure on the final porous structure of the carbon foams in the range 1.5–4.0 MPa by fixing the temperature at 588 K, the solvent proportion at 30 wt %, and the pressure drop rate at 1.5 MPa/s. As shown in Figure 4, the cell density first increased and then decreased, whereas the mean cell diameter continuously increased with increasing initial pressure. As the initial pressure increased, the fluid evaporated less, dissolved more into the molten pitch, and was available for nucleation and cell growth. From eq. (4), it can be definitely noted that the number of bubbles generated increased with  $P$ . Moreover, with increasing dissolved toluene, the viscosity also decreased; this meant that the interval from the viscous flow state to the vitreous state was prolonged. This allowed cells to grow for a longer period into larger size cells.<sup>13,14</sup>

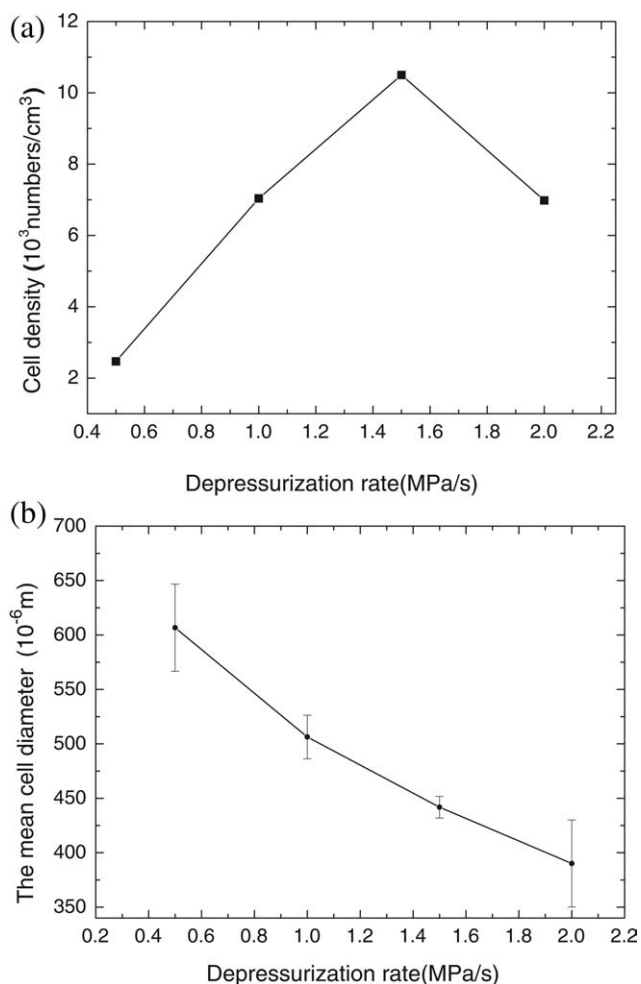
When the pressure was as low as 1.5 MPa, the generated bubbles were fewer and were isolated from each other because of fewer nuclei and insuffi-

cient growth, as shown by Figure 3(c). On the contrary, when the pressure was high, many more nuclei were generated, and they grew into each other to form a three-dimensional networks, where the cell walls were stretched into ligaments with a high orientation, as shown by Figure 3(a).

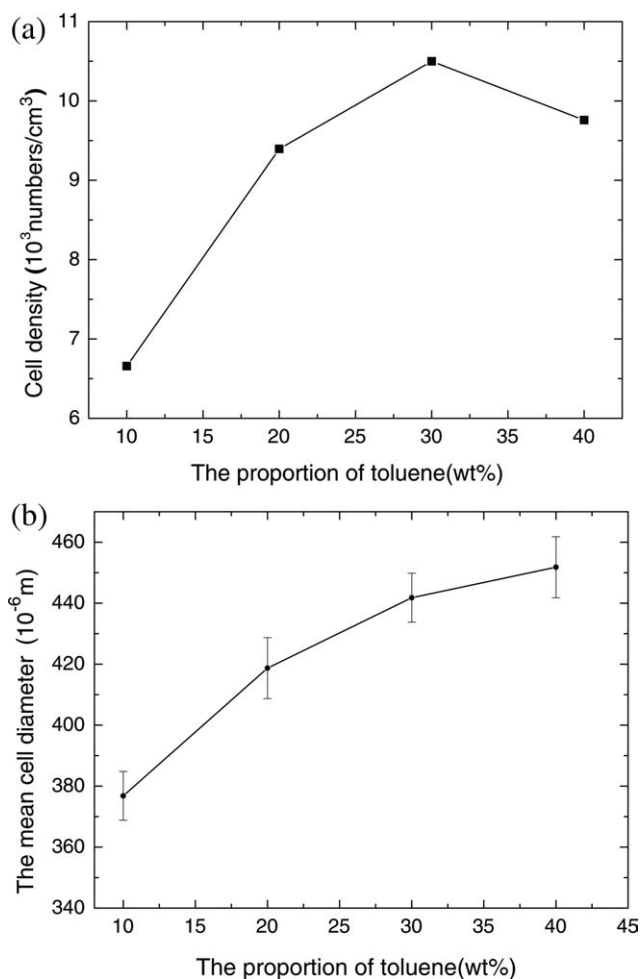
#### Effect of the pressure drop rate

We studied the effect of the pressure drop rate on the final porous structure of the carbon foams from 0.5 to 2.0 MPa/s by fixing the temperature at 588 K, the initial pressure under 3.0 MPa, and the solvent proportion at 30 wt %. Figure 5 shows that the cell density increased first and then decreased, whereas the mean cell diameter declined continuously as the pressure drop rate increased.

The increase in the pressure drop rate gave fewer opportunities for bubble nucleus coalescing; this resulted in a higher cell density. However, too fast a pressure drop rate made the interval for the bubble nucleus to grow shorter than the pitch relaxation



**Figure 5** Effect of the pressure drop rate on the cell density and cell diameter.



**Figure 6** Effect of toluene proportion on the cell density and cell diameter.

time; this resulted in fewer cells. Figure 3(d) shows the foam prepared at 1.0 MPa/s. The bubbles were much larger than those generated at 1.5 MPa/s. The walls were stretched into thin ligaments.

### Effect of the solvent proportion

The solvent proportion directly determines the concentration of solvent dissolved in the molten pitch in eq. (4); this influences the nucleation. The effect of the solvent proportion on the final porous structure of the carbon foams was studied in the range 10–40 wt % at 588 K under 3.0 MPa with a pressure drop rate of 1.5 MPa/s.

As shown in Figure 6, the cell densities increased with toluene proportion up to 30 wt % and then decreased. The increase was easily understood as stated before, whereas the decrease may have been due to phase separation. The separated toluene phase did not obey the homogeneous nucleation theory; this led to the formation of foams with big cells.

Figure 3(e) shows the foam prepared at a lower toluene proportion of 10 wt %, with thick cell walls, a low cell density, and an inhomogeneous cell diameter.

### CONCLUSIONS

In this study, we focused on interpreting the foaming mechanism and optimizing the preparation process of mesophase pitch-based carbon foams with supercritical toluene. The conditions, such as the initial pressure, foaming temperature, pressure drop rate, and solvent proportion, were important factors influencing the structure of the carbon foams; this structure was qualitatively observed under SEM and quantitatively described as the cell density and average pore size. The cell densities showed maximum points, whereas the mean cell diameters increased monotonously with increasing initial pressure, temperature, pressure drop rate, and proportion of toluene. The carbon foam structure was optimized with cell densities of  $10\text{--}16 \times 10^3 \text{ cm}^{-3}$  and cell diameters from 400 to 450  $\mu\text{m}$  where the conditions were as follows: the temperature was 588 K, the initial pressure was 3.0 MPa, the pressure drop rate was 1.5 MPa/s, and the solvent proportion was 30 wt %.

Classical homogeneous nucleation theory was used to explain the effects of the preparation conditions on the cell densities; also, cell coalescence and viscosity could not be neglected.

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