Preparation of Porous Carbon Microspheres

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ABSTRACT: Porous carbon microspheres with good morphology, high yield, and controllable particle size were prepared from phenolic resin. The particle size and pore structure of the carbon microspheres were mainly inherited from their precursors, resol microspheres, which were made through curing emulsified resol in water at 120°C under saturated pressure. The average particle size and specific surface area of the porous carbon microspheres was related to the concentration of resol and polyvinyl alcohol along with the heating program. The carbonization yield to 700°C was 55 wt %. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 798–803, 2006

Key words: curing of polymer; high temperature materials; particle size distribution; spherulites

INTRODUCTION

Carbon microspheres have been drawing much attention for its priority of spherical shape over irregular carbon powders. Mesocarbon microbead (MCMB), as a kind of typical microspherical carbon, has been applied successfully as the anode material of lithium ion batteries.[1–5] Several methods for the preparation of carbon microspheres other than MCMB were reported. The products, according to their properties, can be used as packing material of liquid chromatography,[6] high density monolithic material,[7] adsorption material, and anode material for super electrical capacitor.[8,9] Kodama et al. tried to prepare MCMB by heating mesophase pitch powders in silicone oil.[10] However, it is difficult to produce it commercially because it is hard to prevent coagulation of pitch particles in silicone oil at such a high temperature for lack of suitable surfactant. Yamamoto et al. reported that carbon cryogel microspheres can be synthesized by the sol–gel polycondensation of resorcinol (1,3-dihydroxylbenzene) with formaldehyde in a slightly basic aqueous solution, followed by supercritical drying formaldehyde with carbon dioxide, and pyrolysis in an inert atmosphere. They reported that freeze drying could be used as a less expensive drying method.[11] However, this process is time consuming.

Lu et al. reported that carbon microspheres could be made from commercial resin.[12] In the present work, porous carbon microspheres were prepared from a phenolic resin precursor. The phenolic resin microspheres were made by curing micro-emulsion of resol in water at a high temperature under saturated pressure(saturated pressure means the pressure generated by water itself at the set temperature). The specific surface area and the particle size could be controlled through adjusting the concentration of resol, as well as heating rate. The particle size was also influenced by the concentration of polyvinyl alcohol (PVA). The porous carbon microspheres could be more prospective than general porous carbon as anode material for super electrical capacitor because spheres allow electrolyte to flow more easily among them than irregular powders.

EXPERIMENTAL

Preparation of carbon microspheres

A commercial resol with 85% solid content was used as the raw material. First, the resol was diluted with alcohol into solutions of different concentrations. Then, the resol alcohol solutions were poured into PVA aqueous solutions in the volume proportion of 1:2, emulsified at room temperature for 30 min and heated to 120°C with various heating rates in an autoclave under saturated pressures and cured for 3 h. Then, the cured spheres were filtered, rinsed, and dried.

The dry resin spheres were carbonized at 700°C with heating rate of 5°C/min in nitrogen.

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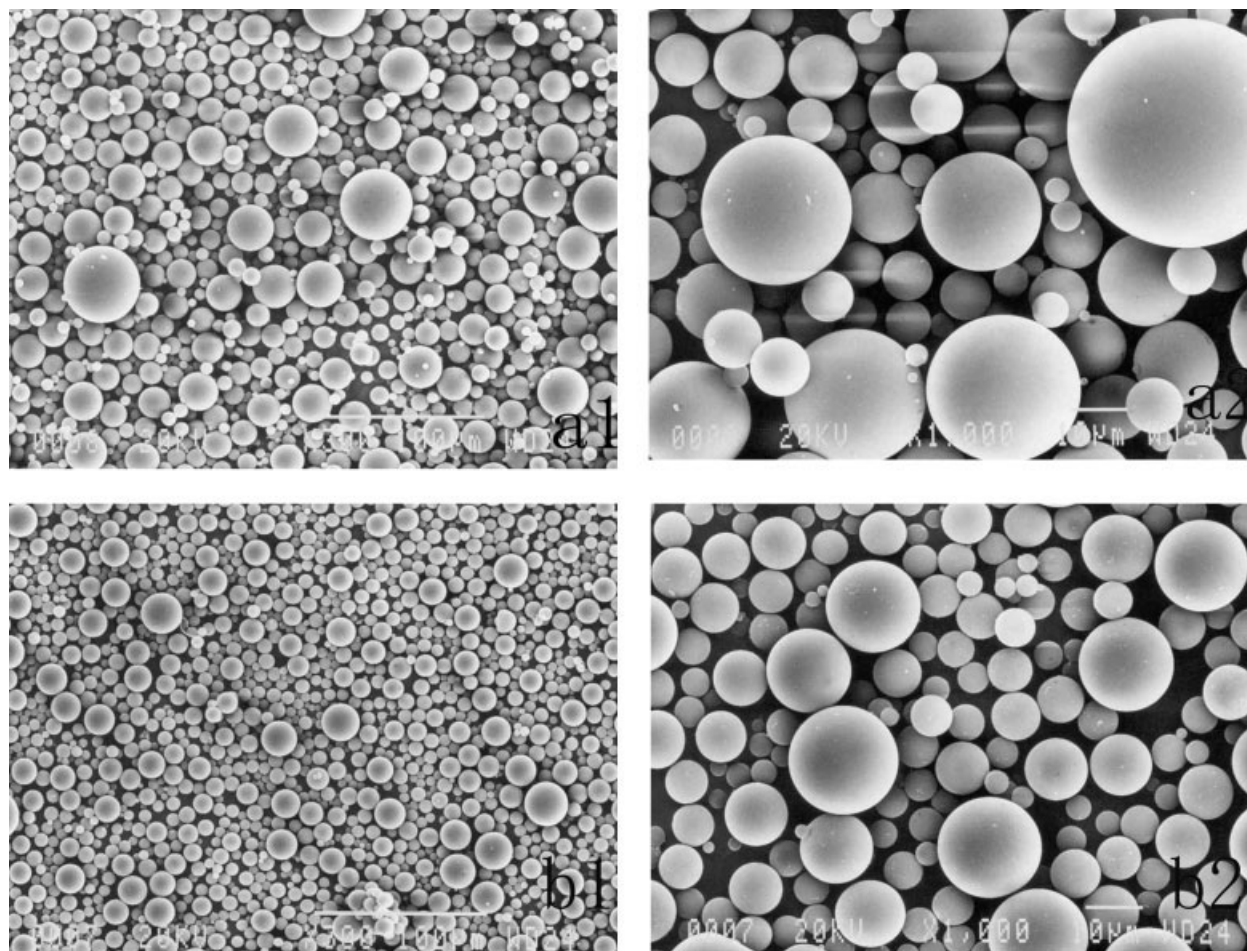
Figure 1 SEM images of carbonized microspheres. a1 and a2: Resol concentration 66%, b1 and b2: Resol concentration 50%, Curing : heated at 1°C/min to 120°C, held 3 h in 1 wt % PVA aqueous solution.

Characteristics of the microspheres

A scanning electron microscope (SEM; JEOL-JSM 25) was used to observe the surface and inner morphology of the carbonized microspheres.
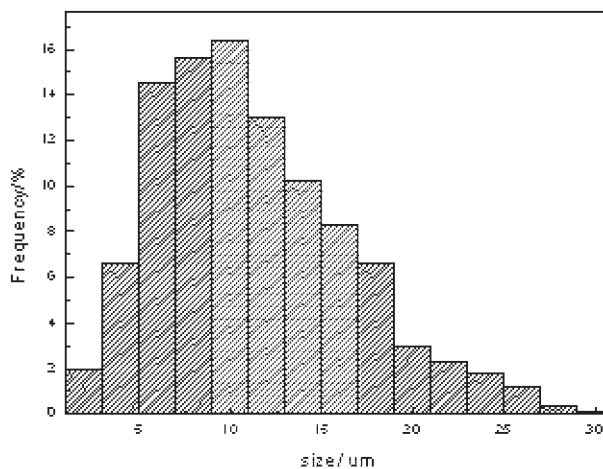
The size distribution of the microspheres was measured on Hydri 2000MU laser diffractometer, during which the microspheres were dispersed into acetone and the volume of a single microsphere was detected by the laser measurement.

The BET-specific surface area of the samples was caculated from their nitrogen adsorption isotherms, and the pore size distributions were determined by applying the Dollimore-Heal method to their nitrogen desorption isotherms.
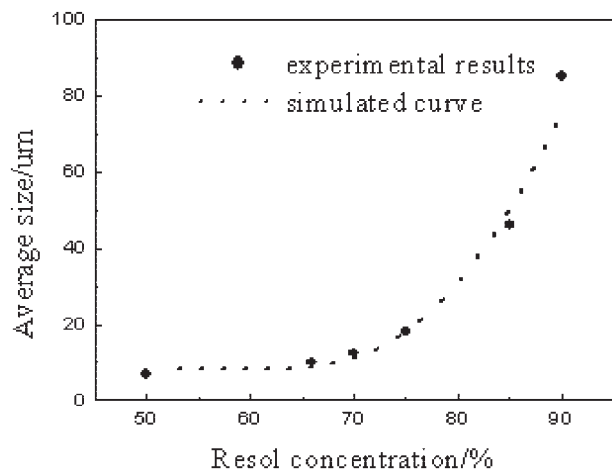
RESULTS AND DISCUSSION

Morphology of the carbonized microspheres

The morphology of the derived carbon microspheres was observed under SEM, and the result is shown in Figure 1. From this it can be noted that the carbon

Figure 2 The size distribution of the carbon microspheres. Resol concentration 66%, 1°C/min to 120°C, held 3 h in 1.0 wt % PVA aqueous solution.

Figure 3 The relationship between the average size of carbon microspheres and the resol concentration. PVA 1.0 wt %.

microspheres were prepared with perfect spherical shape. The precursors of the carbon microspheres were prepared by curing 66 and 50 wt % resol alcohol solutions respectively, in the media of 1.0 wt % PVA aqueous solution at 120°C for 3 h with heating rate of 1°C/min. Figure 2 shows the size distribution of the sample corresponding to the condition of 66 wt % resol concentration. The sizes of the carbon microspheres ranged from 1.0 to 30.0 μm, of which, 65% were distributed between 5.0 and 15.0 μm. The carbonization yield was 55 wt %, while the yield of the resin microspheres from resol was 85 wt %, depending on the polymer content of the raw material. Through SEM observation, it is known that carbon microspheres can be prepared efficiently by this way with high yield and good appearance.

Size controlling of the microspheres

Though the carbon microsphere could be made with perfect appearance and fairly narrow particle size distribution, the control of average particle size is more important for its application. The particle size of the carbon microspheres depended on its precursor microspheres, which was determined by the size of resol drops in the emulsion. It can be known from emulsion knowledge that the size of the emulsified drops is corresponding to the properties of the dispersed phase, dispersant, and the surface active agent, especially viscosity. So, the influence of resol and PVA concentration on particle size was investigated.

Influence of the resol concentration on the particle size

It can be seen from Figure 3 that the concentration of resol had a strong influence on the size of the derived

carbon microspheres. In the figure, the experimental results are shown by the dots. The average size of the microspheres increased with the concentration of resol, and changed rapidly when the concentration of resol alcohol solution was over 75%. The reason could be that, the more the resol was diluted, the lower its viscosity and surface tension, the smaller the liquid drops were. This is corresponding to Lyons-Tobolsky law that describes the concentration dependence of the viscosity of polymer solutions:

$$\eta_{SP} = C_1[\eta]\exp\left(\frac{k'_m[\eta]C_1}{1-bC_1}\right) \qquad (1)$$

where, η_{sp} is the viscosity of a polymer solution,[13–15] C_1 is the mass concentration of the polymer solution, $[\eta]$ represents intrinsic viscosity of the polymer in the solvent, k'_m is martin index, and b is a constant.[13,14]

Set the average size of the spheres is proportional to the viscosity of a polymer solution η_{sp},

$$\bar{d} = K_1\eta_{sp} \qquad (2)$$

where K_1 is a constant.

From eqs. (1) and (2), the following equation can be obtained:

$$\bar{d} = K_1[\eta]C_1\exp\left(\frac{k'_m[\eta]C_1}{1-bC_1}\right) \qquad (3)$$

According to eq. (3) and the experimental data, a simulated equation can be induced as:

$$\bar{d} = 8.4C_1\exp\left(\frac{0.4C_1}{1-0.95C_1}\right) \qquad (4)$$

A curve corresponding to eq. (4) is presented in Figure 3, which fits the experimental data well, meaning the viscosity did have a strong influence on the size of the microspheres.

Influence of PVA concentration on the particle size

Another influential factor to the particle size was the surface active agent PVA. The surfactant acted on preventing liquid drops coalescing by two key components, hydrophilic group and lipophilic group. During emulsification, the lipophilic side was attached to the resol solution and the hydrophilic side remained inside the water. With strong stirring, the resol solution was separated into numerous liquid microspheres in the water. However, the process was dynamically reversible. The liquid microspheres tended to coalesce into each other till being cured. It can be imagined that a certain amount of PVA molecules on a specific unit surface were needed to make a drop stable. Then, the
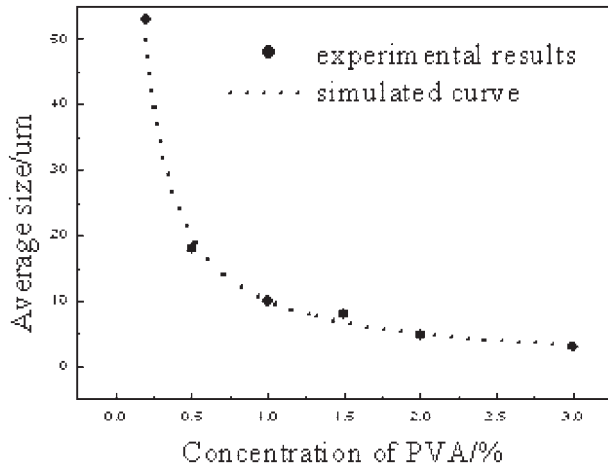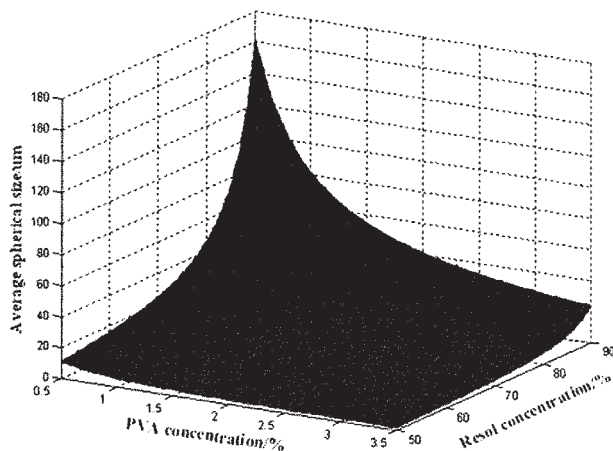
Figure 4 The relationship between the average size of carbon microspheres and the PVA concentration. The Resol concentration is 66 wt %.

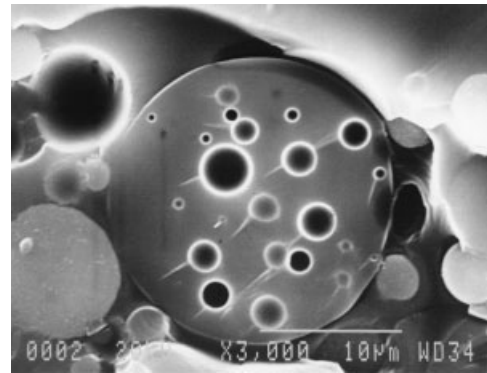**Figure 6** Cross section of the carbonized microspheres.

smaller the spheres, the larger the total surface area, and the more the PVA was needed, in other words, more PVA was needed to make smaller spheres. Figure 4 shows that the average size of the carbonized microspheres decreased as the concentration of PVA increased. Here, resol's concentration and quantity was fixed. So, it is reasonable to assume that, to keep the liquid drops separated, a certain amount of PVA molecules must adhere to their surface. An equation can be gotten to describe the above mechanism as:

$$nm^*\pi\bar{d}^2 = K_2C_2 \tag{5}$$

where m is the amount of PVA molecules on unit surface area, n is the number of the drops in unit volume of the water, C_2 is the mass concentration of the PVA, and K_2 is a coefficient related to resol properties.

If the total volume of resol solution was w in an unit volume of the media, then

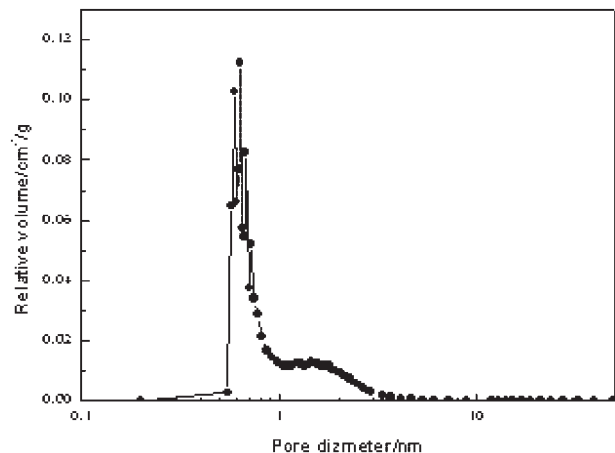$$\frac{n}{6}\pi\bar{d}^3 = w \tag{6}$$

From (5) and (6) we get

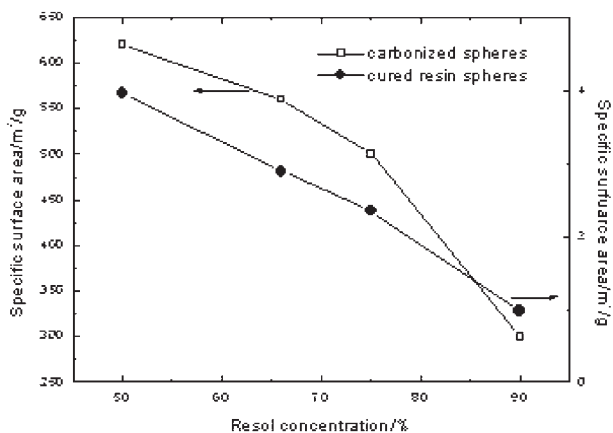$$\bar{d} = \frac{6mw}{K_2C_2} \tag{7}$$

Let

$$K_3 = \frac{6m}{K_2},$$

then

$$\bar{d} = \frac{K_3w}{C_2} \tag{8}$$

Figure 5 The influence of concentration of PVA and resol solution on the average size of derived carbon microspheres.

Figure 7 The pore size distribution of carbon microspheres shown in Figure 1(a).

Figure 8 The dependence of specific surface area of cured and carbonized microspheres on the resol concentration.

Figure 9 The dependence of specific surface area of cured and carbonized microspheres on the curing rate.

From the experimental data shown in Figure 4 and eq. (8), a simulated dotted line curve fitting $\bar{d} = \dfrac{0.1}{C_2}$ (9) can be obtained, as shown in Figure 4, which indicates that the average spherical size was inversely proportional to the PVA concentration when the concentration of resol solution and the volume ratio between resol solution and water was certain.

Relationship of particle size with the concentration of resol and PVA
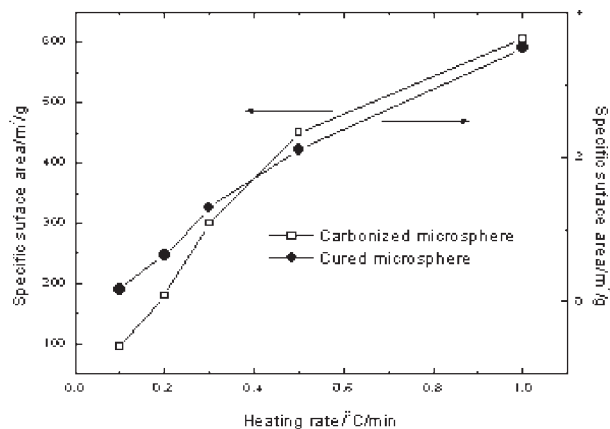
From eqs. (4) and (8), an equation can be gotten to describe the relationship among the average size of the derived carbon microspheres, the concentrations of resol, and PVA,

$$\bar{d} = K_4 \frac{C_1}{C_2} \exp\left(\frac{0.4C_1}{1-0.95C_1}\right) \qquad (9)$$

K_4 was regressed as 0.076 from the experimental data shown in Figures 4 and 5. So we get $\bar{d}=0.076*\dfrac{C_1}{C_2}\exp\left(\dfrac{0.4C_1}{1-0.95C_1}\right)$, (10) from which a three dimensional map can be drawn to show schematically the influence of the concentration of resol solution and PVA in water on the size of carbonized microspheres as in Figure 5.

Specific surface area of the microspheres

The specific surface area would determine the succeeding process and application of the carbon microspheres. Figure 6 shows the transverse structure of the carbon microspheres. There are many macropores (>100 nm) inside the microspheres, which do not contribute to the specific surface area but display the formation of pores. Figure 7 shows the pore size distribution of the carbon microspheres. Most pores con-

tributed to BET surface area were micropores sized from 0.6 to 0.8 nm, while quite a number of them were mesopores ranging from 1.0 to 3.0 nm. Few pores were larger than 3.0 nm. A proper number of mesopores is important as the routeways for ions when the porous carbon microspheres were used as the anode material of super electrical capacitor. Figure 8 shows that the specific surface area of carbonized microspheres decreased when the resin solution became concentrated. Figure 9 shows that BET surface area of carbon microspheres increased when the heating rate was higher. While the specific surface area of the precursor microspheres was low and changed slightly with the preparation conditions. Therefore, it was guessed that the pores in resin microspheres were close, not opened before carbonization. The pores' formation was related to the emulsion process. When the resol solution of alcohol was put into water, it was emulsified into numerous drops. During curing, the emulsified drops coalesced and departed dynamically, forming reverse emulsion inside the drops of resol solution, like (a) and (b) in Figure 10, causing macropores. That means that the macropores were caused by separated phases. The micropores, however, were formed inside the resin phase composing of polymer skeleton, alcohol, and water. The more dilute the resol solution, the
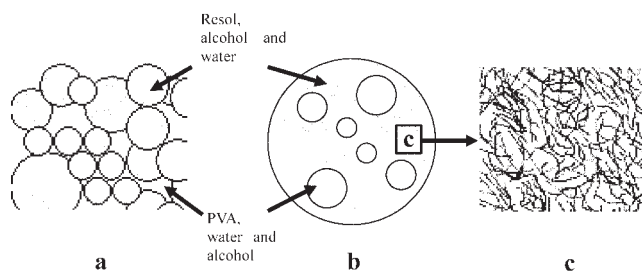
Figure 10 Schematic illustration of dimensional changes during curing of resin microspheres under pressure.

more micropores were kept after the skeleton was cured, which has been illustrated as **c** in Figure 10. As heating rate was increased, the drops cured more rapidly and shrank less, resulting in more micropores.

CONCLUSIONS

Porous resin microspheres can be made by curing emulsion of resol solution directly under pressure. The pores of the resin microspheres were closed as prepared and opened when carbonization. The specific surface area of carbonized microspheres reaches as high as 600 m^2/g without activation. Both average size and specific surface area can be controlled during emulsion curing by the concentration of resol solution, PVA, and the heating program.

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