

Processing of sucrose to low density carbon foams

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Abstract A novel process for preparation low density carbon foams from sucrose has been demonstrated. A resin prepared by heating aqueous acidic sucrose solution when heated in an open Teflon mould at 120 °C undergoes foaming and then setting in to a solid organic foam. The solid organic foam undergoes carbonization in air by dehydration at 250 °C under isothermal condition. Carbon foams thus obtained sintered at temperature in the range 600–1,400 °C showed density in the range 115–145 mg/cc and electrical conductivity in the range 1.5×10^{-5} to 0.2 $\text{ohm}^{-1} \text{cm}^{-1}$, respectively. The carbon foams contain spherical cells of size in the range 450–850 μm and the cells are interconnected through circular or oval shape windows of size in the range 80–300 μm . The carbon foam samples sintered at 1,400 °C showed compressive strength of 0.89 MPa.

Introduction

Carbon foams have been used as catalyst support, electrodes, thermal insulation, light weight structural part, radar absorption material, and filter for molten metals and corrosive chemicals [1–9]. They find application as ablative material in space programs for protection of re-entry vehicles [8]. Reticulated carbon

foams have been used as template for many of the metal and ceramic foams currently used in industry. In addition a number of new applications such as heat exchangers, acoustic panel, electronic heat sinks, EMI shielding, core material for making sandwich structure, ballistic containment cases and fuel cell humidification have been proposed for carbon foams.

Carbon foams have been classified as non-graphitic and graphitic. Non-graphitic foams having low thermal and electrical conductivity have been prepared by carbonizing organic polymer foams through heat treatment. Precursor polymeric materials for non-graphitic foam are phenol formaldehyde, resorcinol formaldehyde, poly urethane, furfural resin, poly vinylidene chloride, poly acrylonitrile and their alloys [10–19]. Klett at the Sandia National Laboratories first produced carbon foam from cork, a natural cellular precursor [20]. Nagle et al. [21] prepared cellular carbon materials from wood by carbonization under controlled temperature and atmosphere. The cellular carbon material thus obtained is further processed to carbon-polymer, carbon-carbon composites and silicon carbide. Graphitic foams have been prepared with tailor made thermal properties in the range of insulating to highly thermal conducting from precursors such as coal and pitch [8–9, 21–27].

Replacement of synthetic materials with agricultural products as feedstock in industrial process getting momentum all over the world. Carbohydrates can be a suitable carbon precursor for preparation of carbon foams. Carbohydrates are considered as hydrates of carbon and represented by general formula $C_x(H_2O)_y$. They easily undergo dehydration and produce carbon. Sucrose is a disaccharide obtained in abundance from sugar cane. Bohme et al. [28] reported a synthesis of

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mesoporous carbon from sucrose. The present work reports preparation of organic foam from sucrose and its subsequent carbonization to low density carbon foams.

Experimental

Sucrose (HiMedia, India) and nitric acid (Merck, India) used were A.R grade. Distilled water was used for preparation of solutions. Flow chart for the process for preparation of carbon foam is shown in Fig. 1. About 50 wt% sucrose solution was prepared in distilled water. The pH of the solution was adjusted to 0.5 using nitric acid. The solution was concentrated by heating on a hot plate until it becomes dark viscous resin. Viscosity of the resin was measured using cone and plate viscometer (Haake RV3). The resin was cast in open rectangular Teflon mould and heated in an air oven at 120 °C for 48 h for foaming and drying. Infrared spectrum of the dried foam sample was

recorded using an infrared spectrophotometer (Perkins Elmer 1600 series FTIR). The dried foam was cut in to pieces of 8 cm × 4 cm × 2.5 cm size for further heat treatment studies. The foam samples were heated in an oven at a rate of 120 °C/h up to 200 °C and then at a rate of 50 °C/h up to 250 °C. The samples were held at 250 °C for 16 h. The foam samples were further heat treated at various temperatures in the range 600–1,400 °C for 1 h in a vacuum furnace at a vacuum level of 1.5×10^{-5} m bar. Heating rate used was 300 °C/h. Density and shrinkage of the foams was calculated from dimensional measurements. Electrical conductivity of the foam samples were measured using precision impedance analyzer (4294A, Agilent Technologies, Japan). Phase analysis of the carbon foams samples were carried out in an X-ray diffractometer (Philips analytical PW 1710) using $\text{CuK}\alpha$ radiation. Surface area of the foam samples were measured by BET method (Sorptomatic 1990, Thermo Fennigan). Samples for surface area measurement were prepared by crushing the foam bodies using mortar and pestle. Microstructure of carbon foam samples was observed in a scanning electron microscope (LEO 1455). Compressive strength of the foam bodies were measured at a loading rate of 5 mm/min in a Universal Testing Machine (Hounsfield, S-sires). Foam samples of 30 mm × 25 mm × 25 mm size was used for compressive strength measurement.

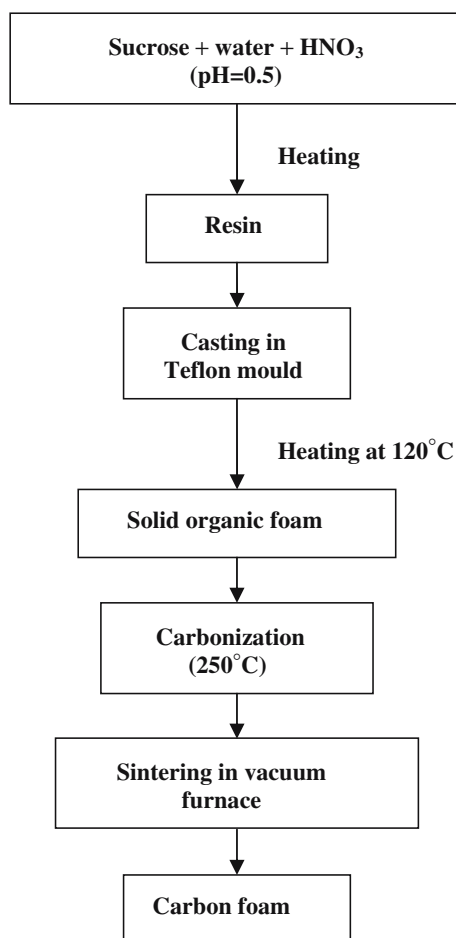


Fig. 1 Flowchart for preparation of carbon foam

Results and discussion

The aqueous acidic sucrose solution when concentrated by heating formed a dark colored resin. The viscosity of the resin at various shear rates measured at room temperature (~ 30 °C) is shown in Fig. 2. Viscosity values of the resin at shear rates in the range 266.2–1,507.8 s^{-1} is in the range of 637–670 MPa s. Time required for 500 g sucrose batch to reach this viscosity values was nearly 45 min. This resin cast in an open Teflon mould when heated in an air oven at 120 °C formed a skin on the surface which restricted further escape of volatiles resulted in slow foaming. The foam on drying set in to a solid (hereafter called as solid organic foam). The resin took nearly 8 h for foaming and 40 h for setting in to the solid organic foam. Figure 3 shows photograph of the solid organic foam showing the skin layer on the surface and a cross-section showing uniform foam structure underneath the skin layer. The skin layer on the surface can be easily removed using a knife. The organic foam had sufficient strength for handling and for minor machining

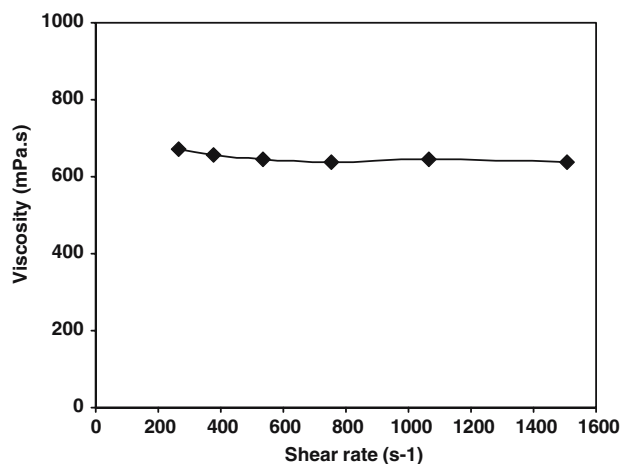


Fig. 2 Viscosity at various shear rate of the resin prepared by heating aqueous acidic sucrose solution

operations. Figure 4 shows SEM photograph of the solid organic foam sample. The foam has a cellular structure and the cells are interconnected through thin membranes. It is clear from the microstructure that some of the membranes are already broken and some others are about to break.

IR spectrum of the solid organic foam sample showed broad peak at $1,065\text{ cm}^{-1}$ corresponding to C–O–C linkage and a low intensity peak at $1,725\text{ cm}^{-1}$ corresponding to ester group. It is well known that sucrose in acidic aqueous medium undergoes hydrolysis to form glucose and fructose and nitric acid oxidizes the glucose and fructose in to a mixture of hydroxy carboxylic acids such as gluconic acid, saccharic acid, glycolic acid and tartaric acid [29]. However, the nitric



Fig. 3 Photograph of solid organic foam showing skin layer on surface and a cross-section showing uniform foam underneath the skin layer

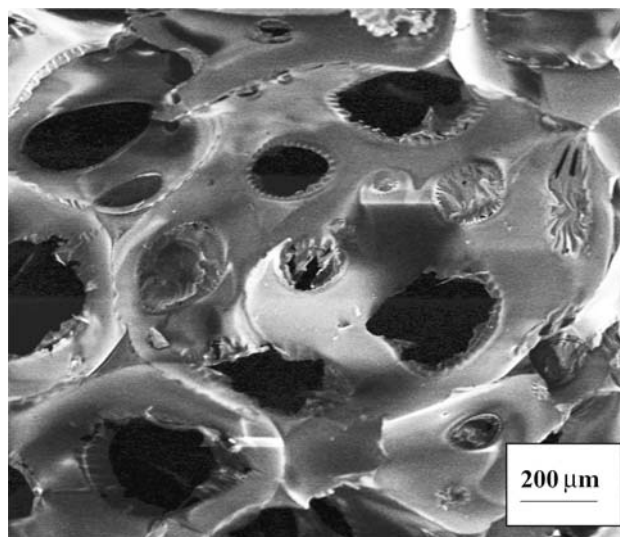


Fig. 4 SEM photomicrograph of the solid organic foam

acid used for pH adjustment in the present case is not sufficient for complete oxidation of the glucose and fructose in to the above hydroxy carboxylic acids. But formation of small amount of the hydroxy carboxylic acids is expected. On concentration of the solution by heating, the carbohydrate molecules and hydroxy carboxylic acid formed by oxidation undergoes polymerization by –OH to –OH condensation and –COOH to –OH condensation to form a resin. The resin cast in an open Teflon mould when heated at $120\text{ }^{\circ}\text{C}$ continues the condensation reactions and set in to a solid organic foam.

Figure 5 shows TGA–DSC plot of the solid organic foam sample. Thermal degradation involves two steps; dehydration of the solid organic foam and oxidation of resulting carbon. Two exothermic peaks were observed in DSC corresponding to the two stages. Weight loss of

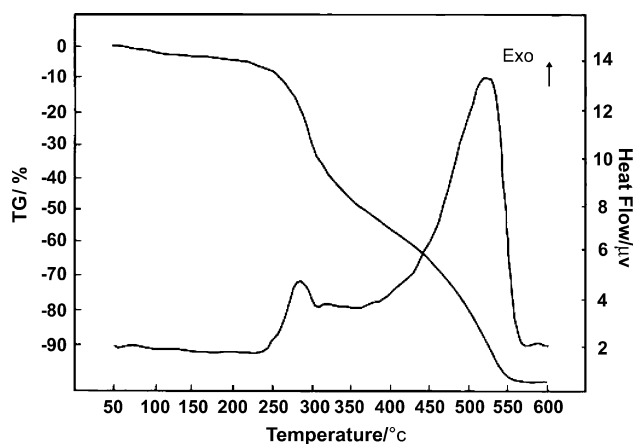


Fig. 5 TGA–DSC plot of the solid organic foam sample

44.8% observed up to 350 °C is attributed to dehydration of the solid organic foam and further weight loss is due to oxidation of the carbon. Figure 6 shows weight loss from large body (8 cm × 4 cm × 2.5 cm) of solid organic foam under isothermal condition at 250 °C in air atmosphere. A weight loss of 23.8% was observed in the initial 1 h. The rate of weight loss decreases with time and reached a near plateau in 12 h. Total weight loss observed at 16 h is 45.5%. That is, dehydration of the solid organic foam can be completed under isothermal conditions at 250 °C for 16 h. The organic foam undergoes isotropic shrinkage during dehydration. Shrinkage observed during dehydration was 43.3 vol%. Major portion of the shrinkage was observed in the temperature range 200–250 °C. Therefore, a slow heating rate of 50 °C/h is used in this temperature range. Most of the membranes connecting the cells in the foam structure were broken during the dehydration stage. Figure 7 shows SEM microstructure of solid organic foam after dehydration. The fragments of broken membrane are clearly seen on the SEM photograph. These membrane fragments vanish during sintering of the foam in vacuum at 600 °C. Figure 8 shows SEM photomicrograph of the foam sample sintered at 600 °C.

Figure 9 shows density and shrinkage of the carbon foam samples sintered at temperature in the range 600–1,400 °C. The dehydrated solid organic foam undergoes further shrinkage during sintering and the shrinkage observed was also near isotropic. Shrinkage of the foam samples increases with sintering temperature up to 1,200 °C and there after remains more or less constant. Shrinkage observed at sintering temperature in the range 600–1,200 °C was 31.15–46.24 vol%, respectively. Density of the carbon foam increases

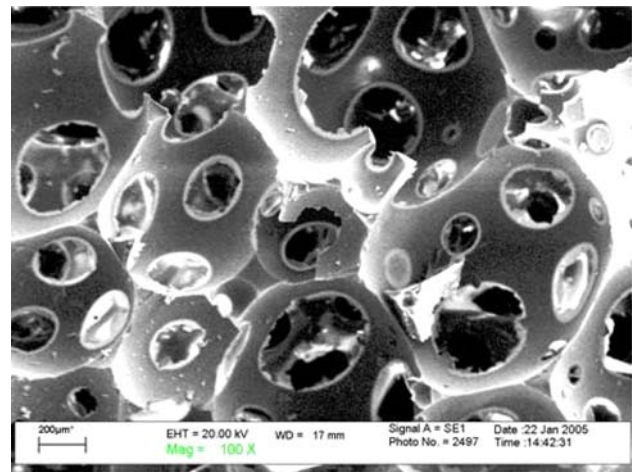


Fig. 7 SEM microstructure of dehydrated solid organic foam

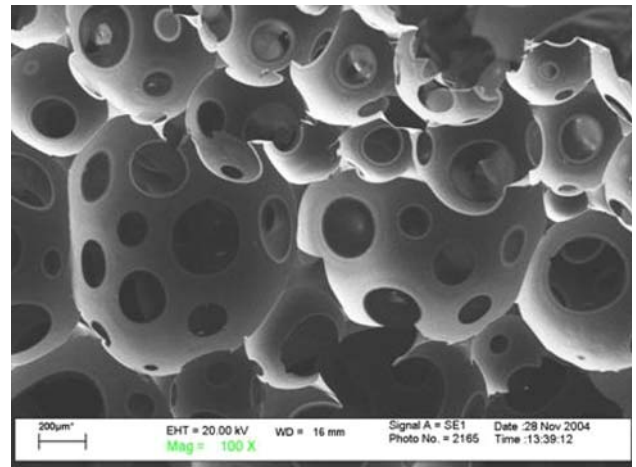


Fig. 8 SEM microstructure of the foam sample sintered at 600 °C

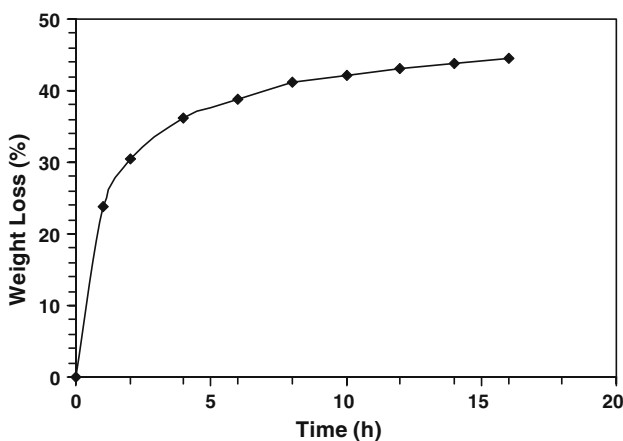


Fig. 6 TGA of large solid organic foam body under isothermal condition at 250 °C (sample size 8 cm × 4 cm × 2.5 cm)

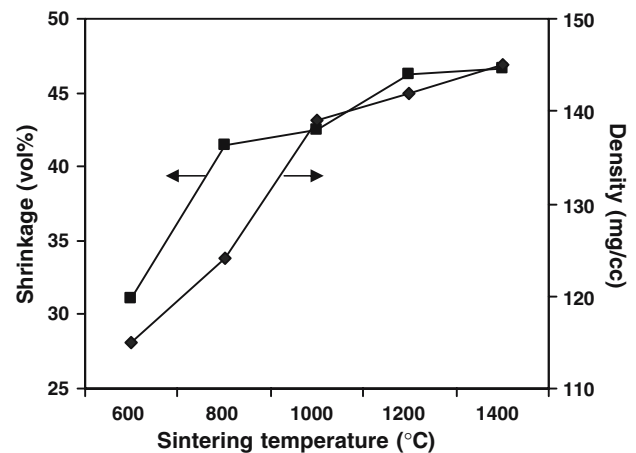


Fig. 9 Shrinkage and density of carbon foam samples sintered at various temperatures

from 115 to 142 mg/cc when sintering temperature increases from 600 to 1,200 °C. After 1,200 °C negligible density increase was observed. Density of the carbon foam sintered at 1,400 °C was 145 mg/cc. No cracks or deformation was observed during sintering. Figure 10 shows photograph of a carbon foam body sintered at 1,400 °C. Surface area of the carbon foam samples sintered at 1,400 °C is 17.3 g/cm³.

XRD analysis of the foam sample sintered at 1,400 °C showed three peaks at 2θ values 22.15, 43.39 and 71.97, which corresponds to crystalline reflections from (002), (004), and (006) planes [30, 31]. The (002) peak is diffuse type and the corresponding d-spacing is 4.09 Å which is far higher than that of graphite (3.334 Å) indicating that no graphite structure has been formed and very little stacking order exists. Figure 11 shows XRD pattern of the carbon foam sample sintered at 1,400 °C.

Figure 12 shows SEM microstructure of the carbon foam sample sintered at 1,400 °C. Microstructure of the foam consists of spherical cells of size in the range 450–850 μm with an average pore size of 650 μm. The cells are completely interconnected through circular or oval shape windows. The windows connecting the cells have size in the range 80–300 μm with an average of 190 μm. Each hemispherical portion of the cells observed in the microstructure showed more than two windows. A maximum of seven windows in a hemispherical portion of the cell can be seen in the microstructure.

Figure 13 shows electrical conductivity of the carbon foams samples sintered at various temperatures. Electrical conductivity of the carbon foam increases rapidly up to sintering temperature of 1,000 °C and then slowly with further increase in sintering temperature.

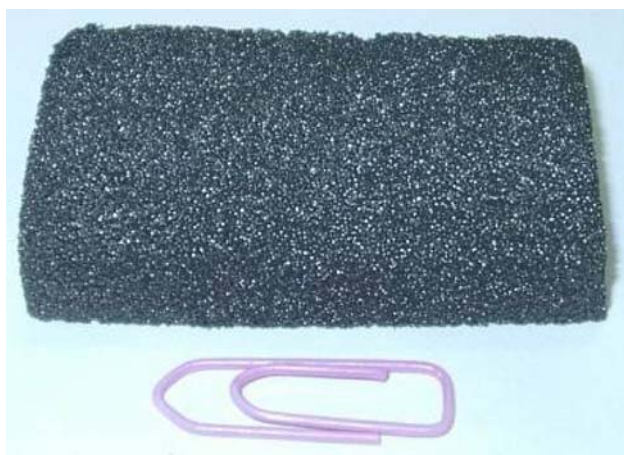


Fig. 10 Photograph of carbon foam body sintered at 1,400 °C

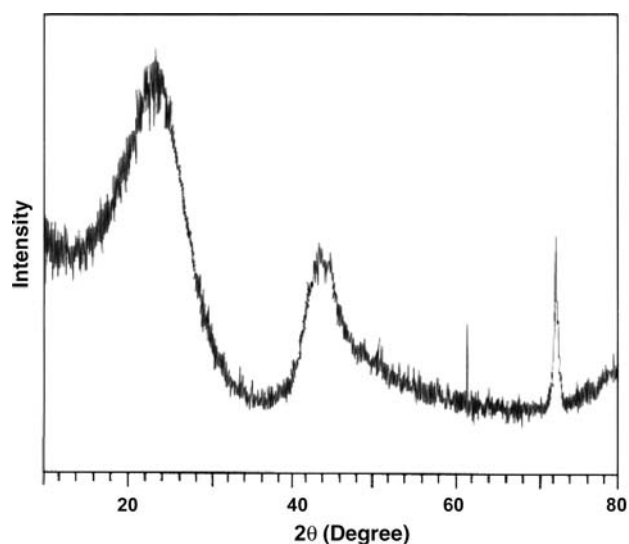


Fig. 11 XRD pattern of the carbon foam sample sintered at 1,400 °C

The carbon foam sample sintered at 600 °C showed very low conductivity of $1.5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ which increased to $0.02 \text{ ohm}^{-1} \text{ cm}^{-1}$ when sintering temperature become 800 °C. Electrical conductivity of the carbon foam samples sintered at 1,000, 1,200 and 1,400 °C are 0.17, 0.19 and $0.20 \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively. It has been reported that high polymers like cellulose, phenolic resin and poly furfuryl resin with some degree of cross-linking on charring produce carbon containing graphite ribbons rather than extensive graphite sheets [32, 33]. In the present case, electrical conductivity of carbon foams is due to the similar graphite ribbon like structure formed by charring of the solid organic foam. Increase in electrical

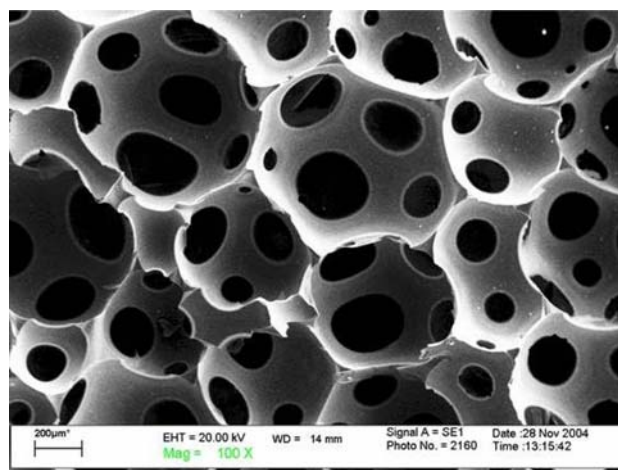


Fig. 12 SEM photomicrograph of carbon foam sample sintered at 1,400 °C

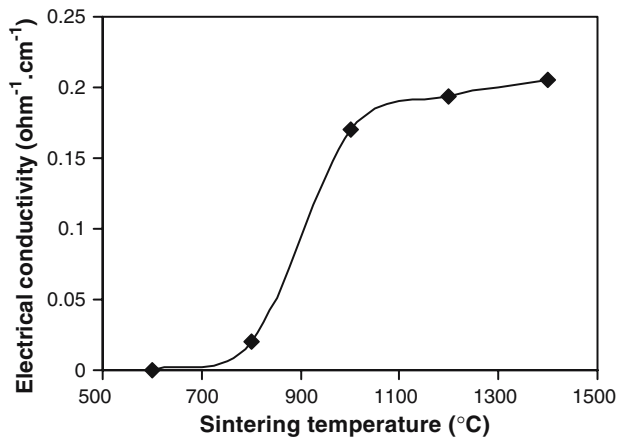


Fig. 13 Electrical conductivity of carbon foam samples sintered at various temperatures

conductivity of carbon foam samples with increase in sintering temperature is attributed to the ordering of these graphite ribbons at higher temperature. The carbon foam sample sintered at 1,400 °C showed an average compressive strength value of 0.89 MPa. Figure 14 shows typical load–displacement curve of the carbon foam sample.

Conclusion

A sucrose-based process for low density carbon foams has been developed. Solid organic foam was prepared by foaming and setting of a resin prepared by heating aqueous acidic sucrose solution. The solid organic foam undergoes carbonization in air atmosphere by dehydration at 250 °C under isothermal condition. The carbon foams sintered at temperature in the range

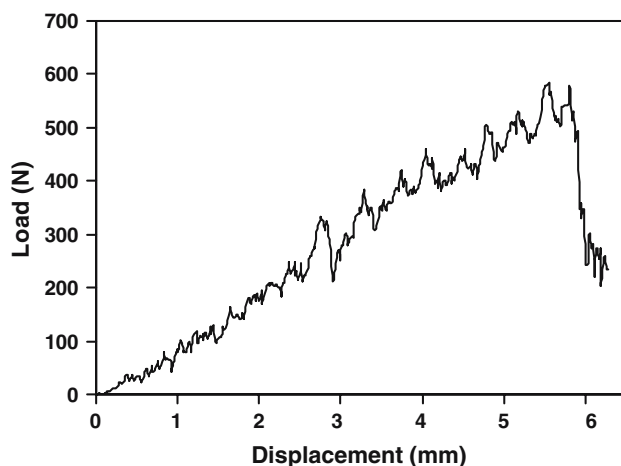


Fig. 14 Typical load–displacement curve of the carbon foam sample sintered at 1,400 °C (density = 145 mg/cm³)

600–1,400 °C showed density in the range 115–145 mg/cc and electrical conductivity in the range 1.5×10^{-5} ohm⁻¹ cm⁻¹ to 0.2 ohm⁻¹ cm⁻¹, respectively. The carbon foams contain spherical cells of size in the range 450–850 μm and the cells are interconnected through circular or oval shape windows of size in the range 80–300 μm. Compressive strength of the carbon foam sample sintered at 1,400 °C is 0.89 MPa.

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