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HIGH SURFACE AREA, HIGH PERMEABILITY CARBON MONOLITHS

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ABSTRACT

The goal of this work is to prepare carbon monoliths having precisely tailored pore size distribution. Prior studies have demonstrated that poly(acrylonitrile) can be processed into a precursor having tailored macropore structure. Since the macropores were preserved during pyrolysis, this synthetic process provided a route to porous carbon having macropores with size =0.1 to 10 μm. No micropores of size <2 nm could be detected in the carbon, however, by nitrogen adsorption. In the present work, we have processed a different polymer, poly(vinylidene chloride) into a macroporous precursor. Pyrolysis produced carbon monoliths having macropores derived from the polymer precursor as well as extensive microporosity produced during the pyrolysis of the polymer. One of these carbons had BET surface area of 1050 m^2/g and about 1.2 cc/g total pore volume, with about 1/3 of the total pore volume in micropores and the remainder in 1 μm macropores. No mesopores in the intermediate size range could be detected by nitrogen adsorption. Carbon materials having high surface area as well as micron size pores have potential applications as electrodes for double layer supercapacitors containing liquid electrolyte, or as efficient media for performing chemical separations.

INTRODUCTION

This work concerns preparation and characterization of carbon monoliths having tailored pore structure from polymer precursors. Monolithic carbons have advantages over the more traditional particulate materials (e.g., activated carbon) for applications involving chemical separations as well as storage of electrical energy. For example, thin carbon electrodes for supercapacitors[1] can be readily prepared from monolithic carbon materials without addition of an inert binder. A binder is needed to process particulate carbons into solid electrodes.

Porous carbon monoliths have been prepared previously from two different classes of polymers. The first class is a chemically crosslinked *thermoset polymer*. A resorcinol-formaldehyde (R/F) thermoset has been processed into open cell porous monoliths, which have then been carbonized by heating them to temperatures around 1000 °C [1, 2]. These R/F carbon aerogels have pores in the micropore (<2 nm) and mesopore (2-50 nm) size range only. The resorcinol-formaldehyde polymer has also been processed into porous carbon precursors via an emulsion based process[3] that incorporates micron scale macropores. The macropores increase the permeability of the carbon to gases and liquids. Both the R/F carbon aerogels and the R/F emulsion derived carbons have nitrogen BET surface areas of several hundred m^2/g. Most of this surface area is present in the mesopores [1,2]. The second class of porous carbon monoliths has been prepared from a non crosslinked *thermoplastic polymer,* poly(acrylonitrile) (PAN)[4, 5]. Preparation of these porous carbons has been adjusted to produce substantial macroporosity in a size range of order 0.1 to 1 μm. The relatively low surface area of these PAN derived carbons,

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typically 10 - 100 m^2/g, made them unsuitable as electrodes for supercapacitors, unless they were activated. The purpose of this work was to prepare porous carbon monoliths having much higher surface area than the PAN derived materials, while maintaining the macroporosity to achieve high permeability for liquids and gasses.

CARBON MONOLITH PREPARATION

To produce high surface area, high permeability macroporous carbon monoliths, we prepared a porous precursor using the solution-gelation process used previously with PAN[4, 5], but we substituted a different polymer, poly(vinylidene chloride) (PVDC). The raw material was a PVDC homopolymer obtained from Solvay Polymers, Inc. It was dissolved in a mixed solvent system selected to minimize any degradation of the PVDC. (This polymer is quite prone to thermal degradation). A solution containing 15 or 20 g/100 ml of the polymer was cooled from about 105 °C to a constant temperature in the range -10 to +50 °C. At that temperature, the solution transformed into a solid gel, indicating formation of an interconnected polymer-rich phase. To remove the solvent mixture from the gel, it was first extracted with a large excess of a very poor solvent for PVDC, isopropanol, and then the isopropanol was removed by supercritical extraction with carbon dioxide at 1500 psi and 34 °C. The product was a porous PVDC monolith having a mass density, 0.145±0.005 g/cc, nearly independent of the gelation temperature. Figure 1a shows that the polymer monolith contained about 2 μm sized macropores.

We have developed a process for carbonizing the porous PVDC precursor without losing the desired macroporosity. The carbonization process involved heating the precursor in an argon atmosphere using a carefully controlled schedule to a maximum temperature of 750 °C. The schedule was designed to substantially crosslink the polymer at a temperature below the polymer's crystal melting temperature (about 200 °C). The crosslinking prevented the macropores in the precursor from collapsing during completion of the carbonization at higher temperature.

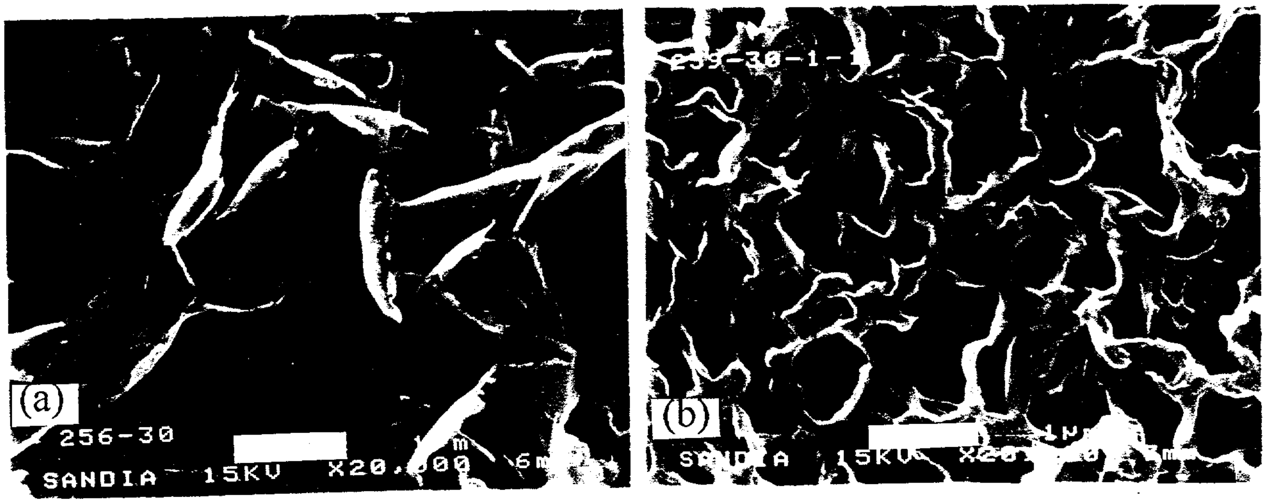

Figure 1. Scanning electron micrographs of a fracture surface of a poly(vinylidene) chloride foam precursor(a) and the PVDC carbon monolith produced from that precursor(b). The carbon has a bulk density of 0.43 g/cc and total pore volume of 1.87 cc/g. The white bars are 1 μm scale markers.

CARBON MONOLITH CHARACTERIZATION

The SEM micrograph in Figure 1b shows that the PVDC derived porous carbon contains approximately 1 μm macropores. The walls of the macropores consist of efficiently interconnected curved flake structures, which are presumed to be remnants of the flake structures in the polymer precursor. Although the bulk density of the PVDC precursor was insensitive to the gelation temperature of the original solution, the density of the carbon decreased substantially when the gelation temperature increased from -10 to +50 °C. The carbon density varied from 0.61 to 0.35 g/cc, which corresponds to a change in total pore volume of 1.2 to 2.4 cc/g, as shown in Table I. The total pore volume was calculated from the bulk density and an estimate of the skeletal density of the solid phase.

Table I
Pore Structure of Carbon Monoliths

	PVDC Carbon	**PVDC Carbon**	**R/F Emulsion Carbon**	**Activated PAN C**
Gelation T (°C)	+50	-10		
Ar BET Surface (m^2/g)	1050	1050	490	450
Bulk Density (g/cc)	0.35	0.61	0.30	0.74
Total Pore V (cc/g)	2.39	1.18	2.82	0.84
Micropore V (cc/g)	0.36	0.36	0.15	0.16
Mesopore V (cc/g)	0	0	0.48	0.03
Macropore V (cc/g)	2.03	0.82	2.20	0.66
Micro + Meso Pore Area (m^2/g)	1300	1300	530	530

The BET surface area of both PVDC derived carbons was the same, 1050 m^2/g. That value was derived from adsorption isotherms for argon at 85 °K. (Nitrogen adsorption gave nearly the same value.) The BET area of the PVDC carbon is about two times higher than that of a typical resorcinol-formaldehyde (R/F) carbon prepared using the emulsion process that produces micron scale macropores (Table I). The PVDC carbon surface area is about two orders of magnitude higher than the surface area of a poly(acrylonitrile) (PAN) derived carbon containing macropores that we prepared in our laboratory using the gelation process with a different solvent system. (Data for that material are not shown in Table I.) In order to produce a surface area in the hundreds of m^2/g in a PAN derived carbon, it was necessary to activate the material[6]. Table I shows that even after activation, the macroporous PAN derived carbon still had less than half the BET surface area of the *unactivated* PVDC carbon. BET surface areas of 450 m^2/g and higher in the PVDC, R/F, and activated PAN derived carbons may initially appear to be inconsistent with the presence of relatively large micron scale macropores. To reconcile that apparent inconsistency, it is important to remember that the average pore size is inversely proportional to the surface area *per unit volume*, not per unit mass.

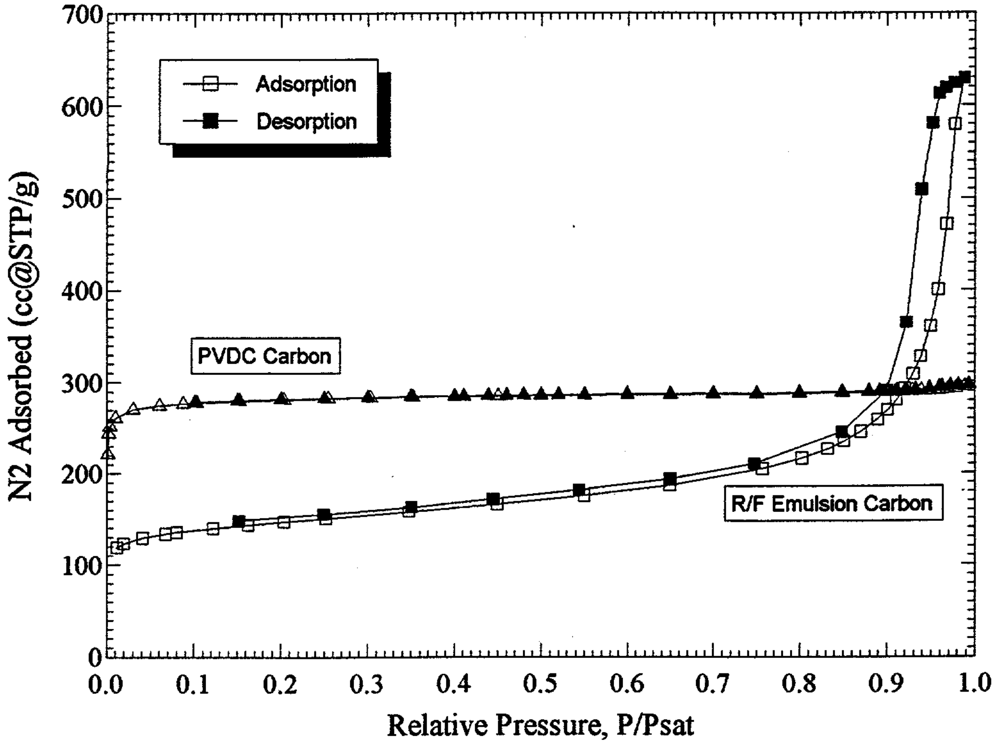

Figure 2. Adsorption and desorption isotherms of nitrogen at 76 °K for the PVDC derived carbon and a typical resorcinol-formaldehyde emulsion derived carbon. The hysteresis in the R/F carbon isotherms is a signature of a substantial volume of mesopores (2 - 50 nm width).

To determine the sizes of the pores that produced the surface area values shown in Table I, we analyzed adsorption isotherms in more detail. Figure 2 shows adsorption-desorption isotherms for nitrogen at 76 °K. The R/F carbon exhibited hysteresis between the adsorption and desorption isotherms, indicative of substantial porosity in the mesopore range (2-50 nm). In contrast, the absence of hysteresis in the isotherms for the PVDC carbons provided no evidence of mesoporosity. To characterize pores in the micro range (<2 nm), we measured adsorption isotherms for argon at 85 °K starting at a very low relative pressure $P/P_{sat} = 1x10^{-6}$. We then analyzed these argon isotherms using a method based on density functional theory [7]. For each material, this analysis produced the volume of slit-shaped pores of different sizes that would produce the same argon adsorption isotherm as the measured isotherm. (In this analysis, the pores are modeled as a non-intersecting set of pores having parallel walls separated by a variable distance, the pore width.) The pore sizes are shown in Figure 3 as a cumulative distribution of pore volume for different pore widths. The pore size distribution was essentially the same for the two PVDC derived carbons prepared using different gelation temperatures. The PVDC carbons had a substantial volume of pores with a width smaller than 1 nm, but no mesopores (in agreement with the conclusion from Figure 2.) In contrast, the R/F carbon had a considerably smaller volume of micropores, but a substantial volume of mesopores (again in agreement with Figure 2.) Finally, the activated PAN derived carbon had a smaller volume of micropores than the PVDC carbon and little mesoporosity. It should be noted that the pore size distribution for the PVDC carbon does not include the micron sized macropores shown in Figure 1b.

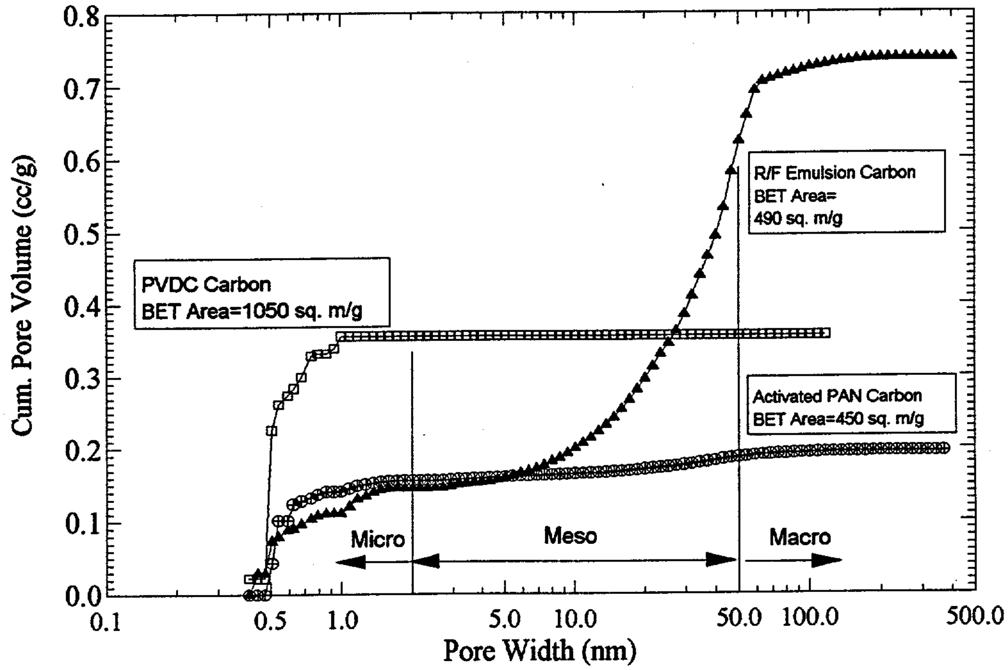

Figure 3. Cumulative distribution of pore volume for slit-shaped pores of different sizes in the PVDC carbon, R/F emulsion carbon, and activated poly(acrylonitrile) derived carbon. The PVDC carbon contains a substantial volume of micropores, but no mesopores.

The volume of micropores and mesopores for each carbon is listed in Table I. The sum of the micro- and mesopore volume was subtracted from the total pore volume in order to estimate the volume of macropores. This table shows that the PVDC carbons, despite having high surface area, have a very substantial volume of the micron scale macropores that will improve their permeability to liquids and gasses. The table also illustrates how the division of total pore volume into the micro, meso, and macro categories can be engineered for different applications by varying the polymer raw material and preparation process.

It should be noted again that the PVDC carbons having BET surface area near 1000 m^2/g have not received any activation. The patent literature[6] indicates that the BET surface area of PVDC derived carbon can be increased to about 1600 m^2/g by activation (partial oxidation) in heated air and nitrogen. It should also be noted that the BET surface area does not accurately define the true surface area of a material that contains micropores. The analysis based on density functional theory [7] provides a more accurate surface area for microporous materials. The surface area of the micro plus mesopores obtained from that analysis is listed at the bottom of Table I. Those values are higher than the BET values, especially for the PVDC derived carbon.

POSSIBLE APPLICATIONS

A high surface area, electronically conductive carbon that is highly permeable to liquids is a candidate for the electrode in supercapacitors[1, 8]. The high permeability will facilitate impregnation with a liquid electrolyte. The high surface area will, in principle, increase the energy stored per unit volume, since the storage mechanism involves formation of a double layer at the interface between the carbon and the liquid electrolyte. It is not clear yet if an effective double layer can be formed inside the micropores present in the PVDC derived carbon. Capacitance measurements on the PVDC carbons are underway and will be reported later.

Another possible application for the PVDC carbon monoliths are chemical separations. These are major applications for conventional activated carbon, which is prepared in a particulate form with particle size ranging from 15 μm to 3 mm. These particulate activated carbons are often packed into beds for purification of liquids and gasses, such as industrial waste emissions, recovery of gasoline vapors in vehicles, and production of industrial gasses such as nitrogen. A bed containing a high surface area carbon monolith may be a more efficient separation medium than a bed packed with particulate carbon due to the absence of any interstices. These serve as a kind of shortcut that can increase the mass transfer resistance between the process stream flowing through a bed and the carbon particles in conventional activated carbon.

CONCLUSIONS

Poly(vinylidene chloride) homopolymer has been processed into porous foam containing about 2 μm pores. This foam has been pyrolyzed into a carbon monolith having macropores about 1 μm in size and about 0.36 cc/g of micropores smaller than 1 nm. Even with no activation, the BET surface area of this monolith is very high, 1050 m^2/g.

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REFERENCES

1. S. T. Mayer, R. W. Pekala, and J. L Kashmitter, J. Electrochem. Soc. **140** (2), 446-451 (1993).
2. F. M. Kong, J. D. LeMay, S. S. Hulsey, C. T. Alviso and R. W. Pekala, J. Mater. Res. **8**, 3100-3105 (1993).
3. W. R. Even and D. P. Gregory, MRS Bull. **19** (4), 29-33, (1994).
4. J. H. Aubert and A. P. Sylwester, J. Mater. Sci. **26**, 5741-5752 (1991).
5. R. R. Lagasse in Extended Abstracts, 21st Biennial Conference on Carbon, (American Carbon Society, 1993) pp. 158-9.
6. D. F. Quinn and J. A. Holland, United States Patent 5,071,820, 1991.
7. C. Lastoskie, K. E. Gubbins, and N. Quirke, J. Phys. Chem. **97**, 4786-96 (1993).
8. F. M. Delnick in Proceedings of Symposium on the Science of Advanced Batteries, edited by D. Scherson, (Electrochemical Society, 1994) in press.