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STRUCTURE AND PERFORMANCE OF CARBON AEROGEL ELECTRODES

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ABSTRACT

The chemistry and physics of small clusters of atoms (1-100 nm) has received considerable attention in recent years because these assemblies often have properties between the molecular and bulk solid-state limits. The different properties can be explained in terms of the large fraction of atoms that are at the surface of a cluster as compared to the interior. Although the synthesis and properties of metal and semiconductor clusters, metallocarbohedrenes, fullerenes, and nanotubes are the subject of extensive investigations, little attention has been paid to cluster-assembled porous materials. This oversight is of particular interest to us since we believe that aerogels are one of the few monolithic materials presently available where the benefits of cluster assembly can be demonstrated. In particular, the unique optical, thermal, acoustic, mechanical, and electrical properties of aerogels are directly related to their nanostructure, which is composed of interconnected particles (3-30 nm) with small interstitial pores (< 50 nm). This structure leads to extremely high surface areas (400-1100 m²/g) with a large fraction of the atoms covering the surface of the interconnected particles. As a result of these structural features, carbon aerogels are finding applications as electrodes in supercapacitors with high energy and power densities.

INTRODUCTION

The use of carbon powders in supercapacitors was patented by Standard Oil of Ohio in 1970 [1]. This technology was subsequently licensed to NEC in Japan who began producing supercapacitors in the early 1980s. Because of their inherently low energy density, such devices were limited to use for memory retention in integrated circuits or clocks. Recently, capacitors using other types of high surface area electrodes (e.g. ruthenium oxide, activated carbon fiber clothes) have been introduced because of their higher energy density [2-6].

Supercapacitors are often referred to as "double layer capacitors" since they store charge at a polarized solid/electrolyte interface, resulting in the storage of energy in the interfacial space charge region. This phenomenon is driven by available surface area of the electrode material and the proper pore size distribution. Carbon aerogels provide an almost ideal electrode material because of their low electrical resistivity ($< 40 \text{ m}\Omega\text{-cm}$), controllable pore size distribution (1-50 nm), and high volumetric surface areas ($\sim 500 \text{ m}^2/\text{cm}^3$).

The exceptionally high conductivity of carbon aerogels, in contrast to loosely bonded carbon powders or activated carbon fiber clothes (ACFCs), is attributable to its monolithic structure which is composed of covalently-bonded carbon particles ($\sim 12 \text{ nm}$ diameter). Electrical conduction takes place by both the drift of the delocalized charge carriers within the carbon particles and the transfer of carriers from one large conducting segment to another by hopping or tunneling [7,8]. In contrast to electrodes made from compacted carbon powders, the activation energy for transport between carbon particles is relatively small in the carbon aerogels, resulting in supercapacitors with potentially high power densities.

The large specific surface areas of carbon aerogels result from the growth and aggregation of crosslinked polymer clusters during the sol-gel polymerization. The resultant surface areas can range from 600-800 m^2/g without the use of any activation procedure. In combination with their high specific surface area, carbon aerogels can be produced with densities ranging from 0.05-1.0 g/cm^3 . As a result, volumetric surface areas of greater than 500 m^2/cm^3 can be achieved. In contrast, ACFCs have higher specific surface areas ($\sim 2000 \text{ m}^2/\text{g}$) but lower bulk densities (0.1 g/cm^3), resulting in volumetric surface areas of only 200 m^2/cm^3 . This parameter is the key to high energy density supercapacitors and provides the rationale for pursuing carbon aerogels as an advanced electrode material.

EXPERIMENTAL

The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [9,10]. Briefly, resorcinol (1,3 dihydroxybenzene) and

formaldehyde were mixed in a 1:2 molar ratio, respectively. Deionized/distilled water was added as the diluent and sodium carbonate as the base catalyst. After stirring to form a homogeneous solution, the mixture was poured into glass vials, sealed, and cured at elevated temperature (50-85 °C). Upon completion of the cure cycle, the crosslinked gels were exchanged with acetone and subsequently dried from supercritical carbon dioxide. This procedure resulted in the formation of monolithic RF aerogels in cylindrical form (25 mm diameter x 60-85 mm long). The monoliths were sliced into 0.5-1 mm thick wafers and pyrolyzed (600-1100 °C) in flowing nitrogen to form carbon aerogels.

In an alternative procedure, carbon aerogel composites were formed by infiltrating a 60-70 % w/v RF solution into a porous carbon paper (Textron Specialty Materials, Lowell, MA). The RF/carbon paper was cured between glass plates in a closed vessel to prevent evaporation. Next, the RF/carbon paper was exchanged into acetone which was subsequently evaporated at room temperature. The RF/carbon paper was then pyrolyzed in an inert atmosphere to give a thin film electrode (~125 µm thick) .

Carbon aerogel monoliths and composites were infiltrated with electrolyte (4-5 M KOH) using an evacuation/pressurization scheme to ensure complete wetting of the porous electrodes. Aerogels with identical composition, diameter, and thickness were separated by a microporous glass filter filled with electrolyte. This sandwich-like assembly was placed inside a Teflon[®] cylinder with non-porous carbon rods (used as current collectors) at either end. A rubber o-ring was used to seal the device, and Exmet[®] metal mesh was used to make electrical contact to the carbon rods. Individual cells were simultaneously charged and discharged between 0.0 and 1.0 V over 1000 second cycles. Current, voltage, and capacity were measured as a function of time using a 16-channel commercial battery tester (Maccor Inc., Tulsa, OK) [11].

RESULTS AND DISCUSSION

The structure and properties of carbon aerogels are largely controlled by three factors: (1) the [Resorcinol]/[Catalyst] (R/C) ratio of the starting solution, (2) the pyrolysis temperature, and (3) chemical activation procedures. The R/C ratio affects the number of RF clusters generated in solution and the size to which they grow. For carbon aerogels synthesized at low R/C values, higher surface areas and better particle interconnectivity are achieved. The specific surface area of carbon aerogels is practically independent of the bulk density for samples prepared *at the same R/C ratio*. Thus, carbon aerogels with a higher bulk density simply have more interconnected particles per unit volume than their low density counterparts. This feature is critical to achieving high capacitance in small volumes.

Figure 1(a) shows the specific capacitance for carbon aerogels synthesized at different R/C ratios. In general, the capacitance ranges from 25-45 F/g with the largest values achieved at low R/C values. This result corroborates BET measurements which show higher specific surface areas, based upon nitrogen gas adsorption, at low R/C values. At a given R/C value, the specific capacitance decreases as the bulk density increases. We attribute this capacitance decrease to a reduction in accessible surface area as more interparticle contacts are made at higher bulk densities.

Figure 1(b) plots capacitance density (F/cm^3) as a function of bulk density for the same carbon aerogels. There is an approximately linear increase in capacitance density with aerogel density in the range from 0-0.5 g/cm^3 . At the highest aerogel densities, the capacitance density begins to plateau at a value of $\sim 26 \text{ F}/\text{cm}^3$. High *capacitance density* is the major advantage of carbon aerogels when compared to activated carbon fiber clothes.

Unlike thermal and acoustic applications of aerogels, it is desirable to use carbon aerogels of intermediate to high density for supercapacitor electrodes. These materials are processed from crosslinked RF gels synthesized at relatively high concentrations (60-70 % w/v). In general, the gel strength increases with concentration to a point where the crosslinked gel can support the capillary forces associated with solvent evaporation from its pores. As such, we have produced thin film carbon aerogel composites which do not require supercritical drying. Figure 2 shows a scanning electron micrograph of a carbon aerogel composite after infiltration, gelation, evaporation, and pyrolysis of an RF solution inside a sheet of carbon paper. The "mud-crack" pattern of the SEM indicates that either (1) the RF gel adheres so well to the carbon fiber that cohesive failure takes place within the gel as it dries or (2) the shrinkage associated with pyrolysis results in cohesive failure within the aerogel rather than at the carbon fiber interface. Capacitance measurements on the carbon aerogel composite give values of $\sim 15 \text{ F}/\text{cm}^3$. While this value is not as high as our best monolithic aerogels, the elimination of the supercritical drying step allows the carbon aerogel composite to be made in a quicker and more cost-effective manner.

Resorcinol-formaldehyde aerogels pyrolyzed at 1050 °C in an inert atmosphere are converted into a nanocrystalline carbon structure. Helium pycnometry reveals a skeletal density of 2.06 g/cm^3 which is much higher than most conventional glassy carbons ($\sim 1.5 \text{ g}/\text{cm}^3$). These data imply that carbon aerogels have very few closed pores within the solid skeleton. Raman data reveal an in-plane microcrystallite size (L_a) of $\sim 25 \text{ \AA}$ for carbon aerogels (R/C=200; 1050 °C) independent of the bulk density [8]. The local structural order, pore size distribution, surface area, and surface functional groups (e.g., -OH, -COOH) depend upon the pyrolysis temperature and atmosphere. Figure 3 shows the capacitance density as a function of pyrolysis temperature for carbon aerogels prepared at R/C=200. In general, the capacitance peaks at a value of ~ 24

F/cm³ for aerogels pyrolyzed at 800-900 °C even though BET nitrogen adsorption measurements reveal higher surface areas at lower pyrolysis temperatures.

The final method for modifying the carbon aerogel structure involves chemical activation. In the carbon industry, activation is commonly achieved by exposing carbon particles or fibers to an oxidizing atmosphere such as steam, air, or carbon dioxide at 500-1000 °C. This procedure usually results in extremely high surface areas (> 1000 m²/g). Carbon aerogels synthesized at R/C=200 were pyrolyzed under nitrogen until reaching 1050 °C, at which time the purge gas was switched to carbon dioxide for 1-4 hours. Next, the tube furnace was switched to nitrogen as it cooled under its own thermal mass. Figure 4 shows the effects of the CO₂ activation. Although the bulk density decreases with activation time, the capacitance density increases ~50% over the control specimen.

BET surface area measurements reveal an increase in specific surface area from ~650 m²/g to ~1200 m²/g after 3 hours of CO₂-activation. If the capacitance density scaled directly with BET surface area, a two-fold increase in the capacitance density would be expected. Gas adsorption analysis reveals that the interconnected carbon particles are microporous with pore diameters centered around 0.6 nm. It is doubtful that this microporosity contributes to electrochemical double layer formation since electrolyte penetration and/or double layer formation are questionable on this scale. We believe that the above data indicate that the double layer is primarily formed at the surface of the individual particles in the mesopore region.

SUMMARY

Carbon aerogels are the first electrically conductive aerogels to be synthesized. Furthermore, these materials are quite pure as compared to other forms of carbon powders or fibers (i.e., they have little inorganic ash content). These attributes have led us to investigate carbon aerogel monoliths and thin film carbon aerogel composites as electrodes in double layer capacitors. These devices store charge at a polarized solid/electrolyte interface, resulting in the storage of energy in the space charge region. This phenomenon is driven by the available surface area of the electrode material and the proper pore size distribution. Carbon aerogels provide an almost ideal electrode material because of their low electrical resistivity (< 40 mΩ-cm), controllable pore size distribution (1-50 nm), and high volumetric surface areas (~ 500 m²/cm³).

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Figure 1. Plots of (a) specific capacitance vs. bulk density and (b) capacitance density vs. bulk density for aerogel electrodes synthesized at various R/C ratios.

Figure 2. Scanning electron micrograph of a carbon aerogel composite electrode. Bulk density equals 0.54 g/cm^3 .

Figure 3. Capacitance density vs. firing temperature for carbon aerogels pyrolyzed in a nitrogen atmosphere. All samples were synthesized at $R/C=200$ and have bulk densities of $0.55 \pm 0.03 \text{ g/cm}^3$.

Figure 4. Capacitance density vs. CO_2 -activation time for carbon aerogels synthesized at $R/C=200$. Note that the aerogel bulk density decreases significantly with activation time.

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