

NOVEL SYNTHESIS OF NANOPOROUS GRAPHITE

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Abstract

Porous carbons with tunable porosity and electrical conductivity have received considerable attention due to their potential application as anodes in lithium ion batteries, electrocatalysts in fuel cells, and high surface area electrodes in electrical double layer capacitors (EDLC). Significant porosity and surface area is easily created by activation of non-graphitizing carbon, yet the materials lack in conductivity. Although graphitic carbons possess high conductivity, they strongly resist activation by traditional methods. EDLC electrodes have been fabricated based on nanoporous activated carbon derived from polyfurfuryl alcohol. In the process, a simple route to synthesize graphitic carbon with nanoporosity has been discovered by subjecting an activated nanoporous carbon derived from a non-graphitizing polymer precursor to high temperature treatment. Porosimetry, helium pycnometry, x-ray diffraction, and transmission electron microscopy, and electrochemical characterization techniques were utilized to thoroughly characterize the materials. Carbons derived from polyfurfuryl alcohol have been demonstrated as suitable electrodes for EDLC. A mechanism of transformation of non-graphitizing to graphitizing carbon is proposed.

Introduction

Development of electrodes for electrical double layer capacitors (EDLC) based on carbon materials has recently garnered tremendous interest. Carbon is environmentally benign and exists in numerous forms; examples are powders, fibers, fabrics, and foams (Frackowiak 2001). Within the operating temperature range of EDLCs carbon is thermally stable and also resistant to acid and base attack. Research in the field of EDLCs is fuelled by applications demanding great energy density, rapid delivery, and longevity (Frackowiak 2001). Chemical batteries cannot meet all of these challenges. Examples of technologies benefiting from EDLC research include hybrid vehicles, uninterruptible power supplies, solar energy storage, and rechargeable power supplies for consumer electronic devices (Wen, Cao et al. 2005). Energy storage in an EDLC is based on separation of charged species in a double-layer formed at the electrode/electrolyte interface (Frackowiak 2001). Thus an effective EDLC should be designed to maximize the area of the electrode contacting the electrolyte solution (Eikerling, Kornyshev et al. 2005).

Nanoporous carbon (NPC) is derived by pyrolysis of polyfurfuryl alcohol (PFA). At 800 °C NPC has intrinsic monodisperse nanoporosity centered at 0.5 nm (Mariwala 1994; Burket 2006). As prepared at 600-800 °C, NPC is entirely nanoporous with a pore volume of $\sim 0.15 \text{ m}^3 \text{ kg}^{-1}$ (Mariwala 1994; Burket 2006). Mesoporosity has been incorporated previously by blending PFA with polyethylene glycol (PEG) prior to pyrolysis (Strano, Agarwal et al. 2003). Physical activation with CO_2 has been shown to further enhance the nano- and mesopore character of the carbon (Marsh 1971; Rand 1971).

Polymer-derived carbons are considered to be either graphitizing or non-graphitizing depending on their tendency to undergo transformation to graphite when annealed at temperatures above 1000 °C (Franklin 1951; Jenkins 1976). Non-graphitizing carbons are globally amorphous, inherently microporous, thermally stable, and resistant to chemical attack (Foley 1995). These unique properties have been attributed to the presence of extensive cross-linking in the precursor, which manifests as a chaotic misalignment of graphene layers in the carbon (Fitzer 1970; Rouzaud 1989; Mariwala 1994; Burket 2006). Over the last sixty years a wealth of knowledge has been accumulated with respect to the structure and properties of non-graphitizing carbon, yet the intrinsic barrier to graphitization is still not entirely understood.

Presently, the synthesis and capacitance of a nanoporous activated carbon derived from a polyfurfuryl alcohol (PFA) precursor is reported. Herein, the surfactant Triton X-100 is demonstrated as a mesopore-forming agent. The porosity of carbons prepared by polymerizing furfuryl alcohol with Triton

X-100 as solvents is evaluated as a function of activation time via methyl chloride adsorption. Gravimetric capacitance was determined. Activated NPC (a-NPC) with tunable porosity is shown to be an effective electrode for EDLC. In an effort to further modify the electrical properties of a-NPC, the carbon was subjected to high temperature treatment (HTT). Evidence of a reduction in the barrier to graphitization is found in a-NPC, as graphitic crystallites were found after annealing an activated, originally non-graphitizing carbon. The evolution of crystallinity in NPC and activated NPC (a-NPC) was examined between 800 and 2000 °C by porosimetry, skeletal density, and x-ray diffraction (XRD).

Experimental

0.048 gm of *p*-toluenesulfonic acid monohydrate (Sigma-Aldrich) was dissolved in 5 ml of Triton X-100 (Sigma-Aldrich) by heating mildly. To this solution, 5 ml of furfuryl alcohol (FA, 99% Sigma-Aldrich) was added. The reaction mixture was stirred magnetically at 10 °C. After polymerization for 48 hours the product was transferred to a quartz boat and pyrolyzed under flowing argon in a quartz tube furnace. The sample was heated at a rate of 10 °C min⁻¹ to 800 °C and held for 1 hour. Thermogravimetric analysis of Triton X-100 indicated no organic or inorganic residue after pyrolysis. The carbonaceous material is derived entirely from the polyfurfuryl alcohol. The carbon was ground and sieved to a particle size of < 38 μm. Activated NPC was prepared in a quartz tube furnace. 0.5 gm of carbon was heated to 900 °C over 1 hour in flowing argon. After 1 hour of soak time the gas was switched to CO₂ and soaked for an additional period of 0.5, 1.5, 2.5, or 3.5 hours. The sample was cooled back to room temperature under argon.

A methyl chloride adsorption isotherm was used to calculate the total pore volume and the average pore size of the carbons according to the Horvath-Kawazoe and the Kelvin models in the nano- and mesopore regions respectively. The skeletal density of the carbons was measured by gas displacement of helium on an AccuPyc 1330 (Micromeritics, Norcross, GA). The apparent surface area of the carbons was calculated utilizing a N₂ isotherm measured on a Gemini 2370 (Micromeritics, Norcross, GA) and the BET equation.

XRD patterns were collected on a Scintag Pad V x-ray powder diffractometer using Cu Kα radiation with a step size of 0.01° 2θ and a count time of 0.5 seconds. Acquisition conditions were 35 kV and 30 mA. A NIST SRM 640c silicon standard was used to correct the line position and broadening of the carbon patterns.

Each electrode was comprised by 85% a-NPC (100 mg), 10% Teflon binder, and 5% by weight acetylene black. After thorough mixing, the powder was pressed into a carbon film at 5000 psi for 20 minutes. The film was cut to form an electrode with an area ~1 cm² and ~0.3 mm thickness. A two-electrode electrochemical capacitor was fabricated by sandwiching a Celgard 5400 membrane (Celgard, Charlotte, NC) between two identical carbon electrodes. Stainless steel mesh was used as the current collector. The cell was immersed in 1 M H₂SO₄ for 2 day before testing began. One of the carbon electrodes acted as both the counter electrode and reference electrode. All measurements were performed on a 263A Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, TN). Cyclic voltammograms (CV) were recorded between -0.5 and 0.5 V at a scan rate of 5 mV s⁻¹. Parasitic faradiac reactions on the current collector were prevented by limiting the potential to 0.5 V.

Results and Discussion

Carbons derived from PFA with Triton X-100 were both nano- (0.16 cm³ gm⁻¹) and mesoporous (0.03 cm³ gm⁻¹) after pyrolysis at 800 °C without modification. A Triton X-100 molecule is comprised of a benzene ring connected to both an eight carbon alkyl chain and a polyethylene glycol chain approximately 10 monomeric units in length. The low-molecular weight PEG acts as a mesopore forming agent, as reported by Strano et al. for pure PEG blended with PFA (Strano, Agarwal et al. 2003). Activation for 0.5 h slightly increased both pore volumes to 0.24 and 0.04 cm³ gm⁻¹, respectively. The nanopore volume grew two-fold to 0.53 cm³ gm⁻¹ after 1.5 h, while the increase in mesoporosity was again minor. Another jump in nanoporosity occurred at 2.5 h, however the mesopore volume now doubled to 0.13 cm³ gm⁻¹. Further activation to 3.5 h produced a relatively small increase in nanoporosity, but the mesopore volume again doubled. At 3.5 h the total pore volume was 1.30 cm³ gm⁻¹, which was broken down into 0.98 cm³ gm⁻¹ of nanopores and 0.32 cm³ gm⁻¹ of mesopores. The mean pore diameter was seen to shift and broaden with

activation time. Initially the pores were 0.54 nm. After 1.5 h of activation they expanded to 0.62 nm and another slight increase to 0.67 nm was found for 2.5 h. The final hour of activation increased the pore diameter markedly to 0.82 nm.

Capacitances were found to lie in the range of 100-200 F gm⁻¹, depending on the degree of activation. Rapid charging without pore resistance was observed. Cyclic voltammograms were nearly rectangular and gave little indication of pseudo-capacitance.

After HTT the accessibility of the probe gas (methyl chloride) to the nanopore structure was reduced at 1200 °C. The nanopore volume fell from 0.16 to 0.04 cm³ gm⁻¹. Further annealing at 2000 °C closed all but a small volume mesopores, 0.02 cm³ gm⁻¹. The skeletal density of a perfect graphite crystal is 2.25 m³ kg⁻¹. The density of NPC at 800 °C was much lower, 1.93 m³ kg⁻¹. This difference was attributed to both the disordered graphene layers containing five and seven-membered rings and the presence of inherent closed porosity incorporated during pyrolysis. Closed pores leave an inaccessible void space in the carbon structure, which contributes to the apparent volume occupied by the carbon, but does not increase the mass. Annealing at 2000 °C caused complete pore closure to occur and the density decreases to 1.4 m³ kg⁻¹.

Crystalline graphite is characterized by a sharp (002) diffraction peak at 2θ=26.5°, which corresponds to a d₀₀₂ of 3.35 Å. The x-ray diffraction patterns of NPC annealed up to 2000 °C clearly indicate that polyfurfuryl alcohol derived carbon is non-graphitizing. The d₀₀₂ decreased from 3.69 Å at 800 °C to 3.51 Å at 2000 °C and the average L_c size grew from 10 to just 15 Å. Significant stacking of the layer planes did not occur.

Carbon activated for 3.5 h was subjected to HTT. Annealing the activated carbon at 2000 °C reduced the pore volume; however 0.72 cm³ gm⁻¹ of pore volume was retained. This included 0.50 cm³ gm⁻¹ of nanopores. If the open pores were converted to closed pores, an accompanying decrease in skeletal density was expected. The skeletal density does linearly decrease with HTT from 2.35 m³ kg⁻¹ for a-NPC at 800 °C to 1.96 m³ kg⁻¹ for a-NPC at 2000 °C. The 0.39 m³ kg⁻¹ drop in density was accompanied by a 0.58 m³ kg⁻¹ loss of pore volume. Whereas with the non-activated samples a pore volume of decrease of 0.17 m³ kg⁻¹ caused a 0.53 m³ kg⁻¹ drop in density. Pore closure is occurred in the activated samples, but not all pores left behind inaccessible void spaces. The decrease in density was disproportionate to the loss of porosity; therefore a portion of the pores must have been converted to a higher density material.

XRD patterns of the annealed activated carbons were remarkably different from their non-activated counterparts. A (002) line for a-NPC at 800 °C was undetectable. Intensity of the (002) peak is related to the stacking of graphene sheets in the layers which form the pore walls. Its absence indicated the pore wall thickness was reduced during activation below the level of detection. The pore walls of the activated carbon were comprised of very few layers or even a single graphene sheet. Annealing the carbon caused the graphene sheets to coalesce and form thicker domains. A broad, low intensity (002) line reappeared in a-NPC at 1800 °C. Further HTT to 2000 °C created a surprising carbon material. A sharp line at 26° indicated graphitic carbon is present in the sample, which was originally non-graphitizing.

De-convolution of the (002) XRD peak for a-NPC at 2000 °C revealed three components: amorphous (A), turbostratic (T), and graphitic (G) (Honda 1967; Oya 1982). The broad amorphous background peak had a d₀₀₂ of 3.66 Å, which was reminiscent of NPC at 800 °C with a 3.68 Å d₀₀₂. The sharp line at 26° was assigned to turbostratic carbon (d₀₀₂ = 3.44 Å) and the shoulder peak at 26.5° was graphitic carbon (d₀₀₂ = 3.37 Å). L_c was calculated to be 276 and 145 Å for the T- and G-components

NPC pyrolyzed at 800 °C was non-graphitizing even when annealed at 2000 °C. The carbon was comprised of disordered of graphene layers. Although disordered, the layers are interconnected and contain non-six-membered rings which prevent realignment of the layers to form long-range graphitic structures. Although high temperature treatment between at 2000 °C was able to introduce further order in the material, it could not be considered graphitic. The pore structure was rendered completely inaccessible as a result of imposing the thermally forcing conditions. Activation dramatically enhanced the carbon porosity and enabled gas molecules to access the entire material. A side effect was the removal of a significant amount of carbon material from the original structure. This is expected to include the portions of the disordered containing five and seven-member rings, which are more susceptible to oxidation than pristine graphene layers. A reduction in the number of graphene layers in the pore wall was also found via XRD. After removal of a part of the highly disordered carbon, the thinner layers were more mobile and able to align themselves into turbostratic domains with long-range order when annealed at 2000 °C. Conversion to graphite was incomplete and thus nanoporous amorphous carbon remained interspersed with

the graphitic structures. This inhomogeneous microstructure is advantageous as the preserved molecular sieving nanopores, with a diameter of 0.82 nm, creates surface area which can provide ready access to the crystallized regions.

Conclusions

Activation of polyfurfuryl alcohol derived nanoporous carbon dramatically enhances its surface area and porosity. The highly porous carbon is an appropriate choice for an electrode in an electrical double layer capacitor. Capacitance up to $\sim 200 \text{ F gm}^{-1}$ has been measured. Activation removes disordered, oxidation-susceptible carbon structures, thereby overcoming the barrier to graphitization in polyfurfuryl alcohol derived nanoporous carbon. Followed by annealing at $2000 \text{ }^\circ\text{C}$ a portion of the once non-graphitizing carbon is now able to graphitize. Nanopores are not completely eliminated after HTT of the a-NPC, which is unlike NPC. The product is an inhomogeneous carbon exhibiting both nanoporosity, a property of the non-graphitizing carbon, and crystallinity, a property of the graphitic component. Research is currently underway to further explore the electrochemical properties of the nanoporous and graphitic composite carbon.

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