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Carbon 44 (2006) 1718–1724

CARBON

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Electrochemical and physical chemical properties of sp^2 carbon microrods

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Received 25 June 2005; accepted 4 January 2006
Available online 11 April 2006

Abstract

We investigated sp^2 carbon microrods resulting from the reaction of lithium with hexachlorobenzene. The material exhibits high surface area (200–340 m^2/g, depending on heat treatment) and a reversible lithium storage capacity in excess of 500 mA h/g. The discharge/charge behavior of the material resembles that of high specific capacity non-graphitic carbon. Without distinguishable plateaus, the reversible intercalation of lithium occurs at a broad potential window below 1 V vs. Li/Li^+. A possible mechanism for the rod formation, based on SEM results, is briefly considered.

Keywords: Battery carbon; Scanning electron microscopy; Adsorption properties; Electrochemical properties

1. Introduction

Carbon-based materials are among the most versatile and widely studied solids. Pure carbon forms the semiconductor graphite, the insulating and ultra-hard diamond, the high surface area amorphous carbons, glassy carbons [1], as well as fullerenes, single- and multi-wall nanotubes and many other "nanoscale" materials [2].

Electrochemical storage applications for some carbon-based materials have been widely investigated and scaled-up to mass production. One example is the use of carbon as the anode for lithium-ion batteries. Commercialized in the 1990s by Sony®, these batteries have become the power source of choice in the high performance portable power market [3,4]. Graphite, as well as hard and soft carbons, have been used extensively as anodes in commercial lithium-ion batteries [3,5].

In the traditional fabrication of battery anodes, polycrystalline micron-sized carbon powders are pressed into dense electrode structures [6]. With the continuing advancements in nanotechnology, there are intensive efforts at determining the effects of particle size on battery performance [4,6,7]. The fact that nanostructured materials perform differently from their bulk counterpart originates from factors such as short diffusion length, high surface to volume ratio, creation of surface defects, and ease of mechanical stress relaxation [8]. It is likely that the control of these features will lead to nanostructured batteries with better performance and stability.

The present paper concerns the synthesis and characterization of a form of carbon which shows very promising behavior for battery applications. Chang et al. recently reported that reaction of lithium with hexachlorobenzene (C_6Cl_6) under vacuum produces carbon rods whose dimensions range from 3 to 15 μm in length and 100–500 nm in diameter [9]. The material was reported to be made up of sp^2 carbon layers stacked in a disordered fashion along the microrod long axis. In this work, we investigated the properties of the carbon microrods with emphasis on its electrochemical and surface area characterization. Their electrochemical stability and capacity were probed, showing that the material is stable and has a lithium charge/

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doi:10.1016/j.carbon.2006.01.007

discharge capacity that exceeds the maximum theoretical capacity of graphite. Although a large irreversible capacity and moderate discharge/charge efficiency might limit applications in traditional lithium-ion batteries, the materials' shape and dimensions make the carbon microrods a promising candidate in three-dimensional (3D) battery architectures [10].

2. Experimental

Carbon microrods were obtained according to the previously reported procedure [9]: C_6Cl_6 (mp 227–229 °C; bp 323–326 °C) and a large excess of lithium metal (cut in small pieces) were mixed together inside a glass tube, which was evacuated and sealed, placed inside a steel pipe, and heated at 250 °C (1–3 h). *CAUTION: C_6Cl_6 is a cancer suspect agent and mutagen; Li is a flammable, moisture-sensitive solid. Both reagents must be handled with care*. The resulting black powder was washed first with toluene to remove organic by-products, and then with isopropyl alcohol and water to remove LiCl and any residual Li. The product was dried at 250 °C for one day. Part of the dry material, labeled CMR-A, underwent further heat treatment at 1000 °C for about 10 h under flowing argon. This heat-treated material was labeled CMR-B. We observed that the material could lose as much as 40–50% of the original weight upon heat treatment.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were obtained with a JEOL JSM 4700J or with a Hitachi 4100 field-emission scanning electron microscope, both equipped with EDAX attachments. In general, no metallization was necessary. Raman spectra were obtained with a Renishaw-1100 Raman microscope. Powder X-ray diffraction (XRD) data were obtained with a home-made instrument using CuKα radiation. Samples were sent to Desert Analytics for elemental analysis (C, H, Cl, Li). Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA7 under a nitrogen atmosphere, using a heating rate of 10 °C/min and a maximum temperature of 900 °C. BET surface area was determined through nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics ASAP 2010 instrument.

The samples for electrochemical tests were prepared by mixing 90 wt% CMR powder with 10 wt% polyvinylidene fluoride (PVDF) in propylene carbonate (PC). Sonication (30 min) followed by vigorous stirring (12 h) resulted in the formation of a black slurry that was dip-coated onto stainless steel meshes (type 3401). The loading was approximately 1 mg for a 1 cm^2 area of the stainless steel mesh. The geometric size of the stainless steel mesh was 0.5 cm^2, which gave 1 cm^2 of effective footprint area considering double-side coating on the mesh. The weight of the samples was measured by a microbalance capable of accurate weight down to 1 μg. The samples were dried at 200 °C under vacuum (10^{-2} Torr) for 3 h before being transferred into an argon-filled glovebox (both moisture and O_2 content in the glovebox were below 1 ppm). The half-cell setup included the as-prepared carbon sample as working electrode, metal lithium foil (>99.95% pure, Aldrich) as counter and reference electrodes, and 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) mixture (1:1 volume ratio) as electrolyte. The stainless steel mesh served as the current collector. Galvanostatic charge/discharge cycles and linear sweep voltammetry were performed to evaluate the electrochemical properties of the samples. All the tests were carried out with an Arbin® multi-channel potentiostat/galvanostat testing system.

3. Results and discussion

Fig. 1 shows SEM pictures of the carbon microrods after the 1000 °C heat treatment. There was no noticeable morphological change on the material before (CMR-A) or after (CMR-B) heat treatment. We observed that the length of the rods ranged from about 5–20 μm. Elemental analysis confirmed that chlorine makes up approximately 5.5% of CMR-A composition. This contribution decreases to about 0.2% upon heat treatment. We observed a similar trend with EDX analysis: 3–6% of Cl in different CMR-A samples, and less than 1% of Cl (and generally absent

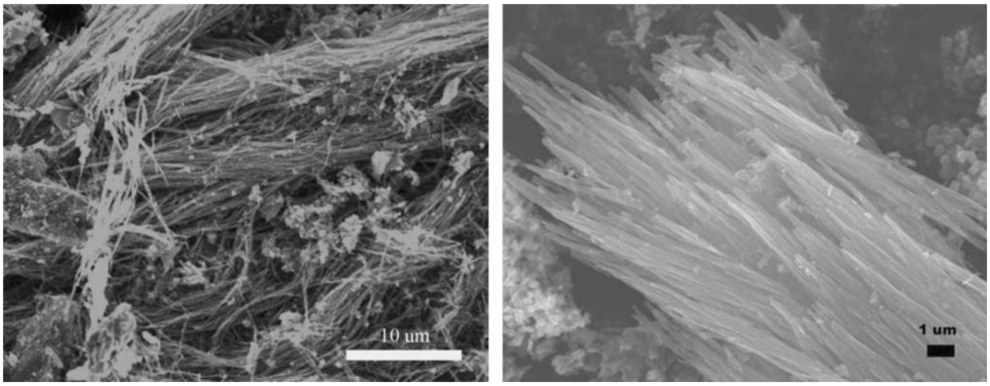

Fig. 1. Scanning electron micrographs of two CMR-B samples at different magnifications.