



Graphitized stacked-cup carbon nanofibers as anode materials for lithium-ion batteries



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ARTICLE INFO

Article history:

Received 28 July 2014

Received in revised form 26 August 2014

Accepted 1 September 2014

Available online 21 September 2014

Keywords:

Carbon nanofibers

High-temperature heat treatment

Anode

Lithium-ion batteries

ABSTRACT

The electrochemical performance as anodes in lithium-ion batteries (LIBs) of graphitized stacked-cup carbon nanofibers (CNFs) with different degree of structural order is investigated by galvanostatic cycling. To this end, two types of commercial CNFs (PR19 and PR24) bearing this microstructure were heat treated in the range of 1800–2800 °C. The discharge capacity provided at the end of cycling, the capacity retention along cycling (cyclability) and the cycling efficiency (charge capacity/discharge capacity) of these nanomaterials improve significantly after heat treatment. Specifically, a progressive increase of the discharge capacity with the growth of the crystallites sizes (L_c , L_a) and the decrease of the structural defects (I_D/I_t) is observed. All heat-treated CNFs exhibit cyclabilities > 80% after 50 cycles and efficiencies > 90%. Particularly outstanding is the performance of PR19-2800 which provides a discharge capacity of 295 mAh g^{-1} with capacity retention up to 88%. The CNFs heat treated at 2800 °C also show good rate capabilities, keeping reversible capacities > 200 mAh g^{-1} at a 2C (744 mA g^{-1}) rate, and > 100 mAh g^{-1} after prolonged cycling (500 cycles) at a 1C rate, clearly outperforming synthetic graphite having micrometric particle size and much larger development of the crystalline structure.

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1. Introduction

Since their introduction in the market by Sony in 1991, lithium-ion batteries (LIBs) have become one of the most important mobile energy storage systems in the world. Nowadays, the demand for high-performance LIBs is rapidly increasing in line with the fast growth of the market of portable electronic devices (mobile phones, tablets, laptop computers, etc.) and the development of the electric vehicle. To satisfy the needs of this market, intensive research has been carried out to improve the overall performance of the LIBs, by increasing both the energy density and power, and extending the lifetime, which are largely governed by the electrode materials. In this respect, the development of new materials, particularly nanomaterials, to replace graphite and $LiCoO_2$, traditionally used as the active materials in anodes and cathodes of LIBs, respectively, is receiving significant attention by the researchers [1–3]. As regards the anode material, carbon nanofibers (CNFs) appear to be a promising candidate [4–20]. In general, the main advantage of CNFs over graphite or other micrometer-sized carbons is their high rate capabilities, providing high reversible capacities even at elevated electric current densities due to their nanometric size which

reduces the diffusion length of the lithium ions in the electrode, thus allowing faster insertion/de-insertion processes, i.e. charge-discharge rate [8,10,15,19,20].

Graphitization thermal treatment is a process consisting in the heat treatment of carbon materials at high temperature (HTT) under inert atmosphere to achieve their transformation into graphite (graphitization) or graphitized materials (graphitization heat treatment). The HTT has been widely applied to CNFs as well, generally leading to materials with higher degree of graphitic order, less structural defects, lower surface area and larger thermal and electrical conductivities [21]. This fine-tuning of the structure and properties of the CNFs often goes in line with an improvement of their electrochemical performance as anodes on LIBs [21]. In this regard, methane-based graphitized CNFs with a high degree of crystallinity, comparable to commercially available micrometer-sized graphite, prepared by HTT in our research group were investigated for this application [18,22,23]. These materials showed excellent capacity retention along cycling and cycle efficiency (> 99%), as well as high discharge capacity (up to 310–320 mAh g^{-1} after 50 cycles), which made them comparable or even superior to commercial graphite [18].

Taking these precedent results into account, the electrochemical performance as potential anodes in LIBs of graphitized stacked-cup CNFs is herein investigated by galvanostatic cycling at different electric current densities. To this end, two different commercial

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CNFs bearing this microstructure with an outer sheath of pyrolytic carbon were heat treated in the range of 1800–2800 °C. The influence of the structural (graphitic order as evaluated from XRD and Raman parameters) and textural (porosity) properties of the graphitized CNFs on their anodic behavior is studied.

Among the different types of as-produced CNFs, the above mentioned stacked-cup, which are commercially available at a reasonable price ($< 0.40 \text{ \$g}^{-1}$) from Applied Sciences, Inc (ASI) are one of the most studied. Specifically, the structural and textural changes showed by these as-produced CNFs during graphitization [24–31], as well as some potential applications, including tests as anodes for LIBs, have been previously reported by other authors [4,7,12,19,32–34]. However, to the best of our knowledge, a combined study correlating the degree of graphitization after HTT with their electrochemical performance as anodes in LIBs has not yet been carried out.

2. Experimental

2.1. Materials

The as-produced CNFs, namely PR-19-XT-PS (PR19) and PR-24-XT-PS (PR24), were obtained from Pyrograf Products Inc. (<http://pyrografproducts.com>), an affiliate of Applied Sciences, Inc. According to the supplier, both types of as-produced CNFs have a stacked-cup microstructure with a hollow core and an outer chemically vapor deposited (CVD) turbostratic layer, which is minimal or negligible for PR24 (average diameters: $\sim 150 \text{ nm}$ for PR19 vs $\sim 100 \text{ nm}$ for PR24). For comparison purposes, synthetic graphite (SG) with micrometric particle size that is currently commercialized for anode in LIBs was also selected.

2.2. High-temperature treatment of the as-produced carbon nanofibers

The graphitization experiments were carried out at 1800, 2200, 2500 and 2800 °C in a graphite electrical furnace for 1 h under argon flow. The heating rates were 25 °C min^{-1} from room temperature to 1000 °C, 20 °C min^{-1} in the range 1000–2000 °C and 10 °C min^{-1} from 2000 °C to the target temperature. The graphitized materials thus prepared were identified by the as-produced CNFs designation, followed by the treatment temperature, e.g. PR19-1800, PR24-2200, etc.

2.3. Characterization techniques

The diffractograms were recorded in an X-ray powder diffractometer as described elsewhere [35]. For each material, three diffractograms were obtained, using a different representative batch of sample for each run. The mean interlayer spacing, d_{002} , was evaluated from the position of the (002) peak applying Bragg's equation. The mean crystallite sizes, L_c and L_a , were calculated from the (002) and (110) peaks, respectively, using the Scherrer formula, with values of $K=0.9$ for L_c and 1.84 for L_a [36]. The broadening of diffraction peaks due to instrumental factors was corrected with the use of a silicon standard. Typical standard errors of the XRD parameters are $< 4\%$ and $< 9\%$ of the reported values for L_c and L_a , respectively; the d_{002} values are much more precise, with standard errors of $< 0.03\%$. L_a could not be calculated for the as-produced CNFs, PR19 and PR24, due to the low intensity and signal-to-noise ratio of the (110) peaks. Raman spectra were obtained in a Raman microspectrometer as described previously [37]. The intensity I of the Raman bands was measured using a mixed Gaussian–Lorentzian curve-fitting procedure. The relative intensity of the Raman D-band I_D/I_t ($I_t = I_D + I_G + I_{D'}$) was calculated with standard errors lower than 5%. The commercial SG was also

analyzed for comparative purposes. These XRD and Raman parameters are used in this study to evaluate the degree of structural order of the materials [38].

The textural properties of the materials were determined by N_2 adsorption-desorption at -196 °C in a volumetric adsorption system. Before measurements, the samples were degassed overnight at 120 °C . The specific surface areas, S_{BET} , were calculated by applying the Brunauer-Emmett-Teller (BET) method, taking 16.2 nm^2 for the cross-sectional area of the nitrogen-adsorbed molecule.

2.4. Cell preparation and electrochemical measurements

The electrochemical measurements were carried out in two-electrode Swagelok-type laboratory cells by galvanostatic cycling. Metallic lithium discs of 12 mm of diameter were used as counter-electrodes. To prepare the working electrodes, the active material (92 wt.%) and the polyvinylidene difluoride (PVDF) binder (8 wt.%) were mixed and stirred vigorously in the minimum amount of 1-methyl-2-pyrrolidone solution (NMP). The slurry was then dried under vacuum at 120 °C for 24 h and the solid thus obtained was ground in an agate mortar. Afterwards, an small amount of this composite (active material + binder) was deposited onto a copper disc of 12 mm of diameter and a thickness of $25 \text{ }\mu\text{m}$ (composite loadings of 1.77 to 3.54 mg cm^{-2} for CNFs-based electrodes, and 3.54 to 8.84 mg cm^{-2} for SG-based electrodes) and a few drops of NMP were added. The slurry thus formed was homogeneously spread over the Cu disc with a metal bar and dried under vacuum at 120 °C for 2 h. Finally, the electrode was hydraulically pressed at a pressure ca. 90 kPa and the cell assembly was carried out in a dry box under argon atmosphere with oxygen and water contents below 0.1 ppm. Two glass micro-fiber discs, impregnated with a few drops of a solution of the electrolyte (1 M LiPF₆ in EC:DEC, 1:1, w/w), were used as separators between the counter (metal lithium) and working (CNFs-based or graphite-based) electrodes. The galvanostatic cycling was carried out in the 2.1–0.003 V potential range at C/10 ($C = 372 \text{ mA g}^{-1}$) using a potentiostat/galvanostat. Moreover, the study of the rate capability of the PR19-2800 CNFs and SG was also conducted, cycling in the same voltage range at C/10, C/5, C/2, C, 2C and back to C/10 during 10 cycles for each one, as well as a prolonged cycling (500 cycles) at a 1C rate.

3. Results and discussion

3.1. Anodic performance of as-produced and heat-treated CNFs at a C/10 rate

Initially, the as-produced and heat-treated CNFs were galvanostatically cycled (50 cycles) at a low electric current density (C/10 rate). All the relevant electrochemical parameters thus obtained are registered in Table 1. From a general perspective of this data, it can be concluded that the HTT of the CNFs leads to a remarkable improvement of the capacity retention along cycling at even the lowest temperature of 1800 °C (49% for PR19 vs 87% for PR19-1800). Furthermore, the discharge capacity provided by these materials after 50 cycles tends to increase as the treatment temperature increases (175 mAh g^{-1} for PR19-1800 vs 295 mAh g^{-1} for PR19-2800) reaching values larger than that delivered by SG graphite (197 mAh g^{-1}). Surprisingly, the heat treatment of the as-produced CNFs at 1800 °C results in a slight decrease of the discharge capacity (193 mAh g^{-1} for PR19 vs 175 mAh g^{-1} for PR19-1800). No significant variations of the irreversible capacity (%) are observed after the HTT of the as-produced CNFs. In any event, these values are unusually large as compared to other graphitic materials, such as for example the SG graphite. These results will be further discussed in detail by studying the influence of the structural and textural

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