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Graphitized biogas-derived carbon nanofibers as anodes for lithium-ion batteries

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ABSTRACT

The electrochemical performance as potential anodes for lithium-ion batteries of graphitized biogas-derived carbon nanofibers (BCNFs) is investigated by galvanostatic cycling *versus* Li/Li$^+$ at different electrical current densities. These graphitic nanomaterials have been prepared by high temperature treatment of carbon nanofibers produced in the catalytic decomposition of biogas. At low current density, they deliver specific capacities comparable to that of oil-derived micrometric graphite, the capacity retention values being mostly in the range 70-80% and cycling efficiency ∼ 100%. A clear tendency of the anode capacity to increase alongside the BCNFs crystal thickness was observed. Besides the degree of graphitic tri-dimensional structural order, the presence of loops between the adjacent edges planes on the graphene layers, the mesopore volume and the active surface area of the graphitized BCNFs were found to influence on battery reversible capacity, capacity retention along cycling and irreversible capacity. Furthermore, provided that the development of the crystalline structure is comparable, the graphitized BCNFs studied show better electrochemical rate performance than micrometric graphite. Therefore, this result can be associated with the nanometric particle size as well as the larger surface area of the BCNFs which, respectively, reduces the diffusion time of the lithium ions for the intercalation/de-intercalation processes, i.e. faster charge-discharge rate, and increases the contact area at the anode active material/electrolyte interface which may improve the Li$^+$ ions access, i.e. charge transfer reaction.

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1. Introduction

Political, scientific and social sectors of modern society agree about the need for reducing the widespread use of fossil fuels as energy resources which has made the global economy fully-dependent on them. This approach is the result of the growing concern about the non-renewable nature of these resources with inevitably end reserves and the environmental pollution associated with their utilization. To tackle the challenge of decreasing the dependency on fossil fuels, the attention has been focused on the exploitation of renewable energy sources for electricity generation and the implementation of the electric vehicle (EV), which require of highly-efficient electrical energy storage/supply (EES) systems [1]. Among them, lithium-ion batteries (LIBs), which are the energy source for most of the mobile electronic devices (laptops, smartphones, tablets, etc.), with a global market value of 17.6 billons $ USA in 2013 [2], are being used in some stationary large scale EES systems from wind and solar energies which are extremely discontinuous and stochastic [3]. Moreover, LIBs have been scaled-up for powering EVs. In this context, the development of long-life, environmentally friendly, low-cost, high-power and high-energy density LIBs to meet the needs of these applications (e.g., more autonomy and faster recharges for EVs) is a subject of great interest for the scientists in the 21st century [4].

Given that the overall performance of LIBs is largely governed by the electrode active materials, the development of new ones, particularly nanomaterials to replace those of micrometer size, which are currently used, is receiving significant attention by the researchers [5]. The main advantages of nanomaterials over micrometer-sized materials are associated with the reduction of the solid-phase diffusion time of the lithium ions (Li$^+$), thus allowing faster intercalation/de-intercalation processes, i.e. faster charge-discharge rate, and the increase of the area at electrode/electrolyte interface which may improve the Li$^+$ access (charge transfer reaction) [6]. As a result of these two effects, both the power and the energy of the battery would be improved.

Focusing on the anode, graphite is nowadays the active material of choice *par excellence* in commercial LIBs. This fact is due to economical (easily accessible and low cost) and operational (relatively high capacity/energy density, long cycle life and low

Li+ intercalation/de-intercalation potential) reasons, particularly, in comparison with other non-carbon materials [7]. However, the anode of graphite shows relatively low charge rate which limits the battery power density. To overcome this drawback, different types of nanomaterials [8], including nanocarbons such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, etc. [9] have been investigated as anodes for LIBs. Among them, CNFs, specifically graphitized CNFs, have been successfully tested [10–16]. The graphitization process of CNFs by heating at high temperature (HTT), under inert atmosphere, involves the increase of the graphitic tri-dimensional order and the electrical conductivity accompanied by a decrease of the porosity and the surface area [17,18]. This fine-tuning of the structure and properties of the CNFs was in line with an improvement of the electrochemical performance as anodes on LIBs [17]. In this respect, graphitized stacked-cup CNFs and graphitized methane-derived CNFs that were prepared in our research group by HTT [19], were further investigated for this application [18,20]. These nanomaterials showed good performance in terms of specific capacity, capacity retention along cycling and cycling efficiency, even outperforming synthetic graphite having micrometric particle size, particularly as regards battery charge-discharge rate.

Based on these precedent results, it can be concluded that graphitized hydrocarbon-derived CNFs might be valuable nanomaterials to be used in LIBs. However, it is important to consider that, like graphite (whose main precursor is petroleum coke), they have been obtained from non-renewable energy sources. In an attempt to find an ideal anodic material from the points of view of efficiency and source, graphitized biogas-derived carbon nanofibers (BCNFs) are herein considered, for the first time. Biogas is a renewable energy source which is currently used in co-generation combustion plants for the production of heat and electricity. Nevertheless, the exploitation of biogas for different applications seems to be an interesting option (i.e. the catalytic decomposition of biogas to simultaneously produce syngas and BCNFs [21]), particularly when considering its renewable origin.

In this work, the electrochemical performance as potential anodes for LIBs of graphitized BCNFs was investigated by galvanostatic cycling *versus* Li/Li+ at different electrical current densities. These graphitic nanomaterials have been prepared by HTT of BCNFs produced in the catalytic decomposition of biogas as reported previously [21,22]. The anodic behavior of different graphitized BCNFs is discussed in terms of battery reversible capacity, irreversible capacity in the first cycle, retention of capacity along cycling and cycle efficiency by considering the influence of structural (graphitic order as evaluated from XRD parameters) and textural (surface area, pore volume) properties. The mechanism of Li+ ion intercalation/de-intercalation into/from these novel nanomaterials is also analyzed.

2. Materials and methods

2.1. Graphitized BCNFs: source and preparation

Five different BCNFs from the catalytic decomposition of biogas were heat treated in the temperature interval of 2600–2800 °C for 1 h in argon flow, by using a graphite electrical furnace. The graphitized BCNFs (25 in total) thus prepared were named by adding a suffix with the temperature in the BCNFs precursor designation (e.g. BCNF1-6), such as BCNF1-6/2600. The experimental set up and BCNFs characteristics can be found in [22]. Furthermore, a description of the production and composition of the BCNFs that are used in this work as precursors is provided (see Table S1 in the Electronic Supporting Information). For simplicity, the original graphitized BCNFs designation (e.g. BCNF1-6/2600) has been abbreviated in this paper (e.g. BCNF16/26).

2.2. Characterization techniques

The interlayer spacing, d_{002}, and the mean crystallite sizes along a, L_a, and c, L_c, axes are used to evaluate the degree of structural order of the graphitized BCNFs [23]. They were calculated from the X-ray diffractograms which were recorded in a Bruker D8 powder diffractometer as described elsewhere [24]. The d_{002} was determined from the position of the (002) peak by applying Bragg's equation while the L_c and L_a were calculated from (002) and (110) peaks, respectively, using the Scherrer formula, with values of K = 0.9 for L_c and K = 1.84 for L_a [25]. Typical standard errors of the XRD parameters are < 3% and < 5% of the reported values for L_c and L_a, respectively; the interlayer spacing values are more precise, with standard errors of < 0.06%.

The textural properties of the graphitized BCNFs were measured by N_2 adsorption-desorption at −196 °C in a Micromeritics ASAP 2420 volumetric adsorption system. Before measurements, the samples were degassed overnight at 250 °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. Total pore volumes (V_t) were determined by the amount of N_2 adsorbed at p/p^o = 0.97. Mesopore volumes (2–50 nm) were calculated from the cumulative pore size distributions obtained by applying the DFT (Density Functional Theory) method to the N_2 adsorption isotherms (p/p^0 = 0.97).

For comparison purposes, a synthetic graphite (SG) with micrometric particle size that is currently commercialized for anode in LIBs was also characterized by these techniques.

2.3. Cell preparation and electrochemical measurements

To carry out the electrochemical study of the graphitized BNCFs and SG graphite of reference, two-electrode (working + counter) Swagelok-type laboratory cells were used. To prepare the working electrode, firstly the graphitized BCNFs (active material, 80 wt.%) and the polyvinylidene fluoride (PVDF) binder (20 wt.%) were mixed in 1-methyl-2-pirrolidone (NMP) solution. The slurry was dried at 60 °C for 24 h. Afterwards, a small amount of this composite (active material + binder) was deposited onto a copper disc (12 mm of diameter and 25 μm of thickness) and a few drops of NMP were added. Then it was dried at 120 °C under vacuum for at least 2 h. Finally, it was pressed twice with a hydraulic press at 45 MPa to obtain the working electrode. The electrode load (active material + binder) was calculated by weight difference, being in the range 3.5 − 14.5 mg cm^{-2}. A metallic lithium disc of 12 mm of diameter was used as counter electrode. The assembly of the cell was carried out in a dry box with O_2 and H_2O contents below 0.1 ppm. The electrodes were separated by two micro-fiber glass discs impregnated with a few drops of the electrolyte solution, 1 M $LiPF_6$ in ethylene carbonate (EC):diethyl carbonate (DEC), 1:1, w:w.

The electrochemical measurements of the cells were conducted in a Biologic multichannel VMP2/Z potentiostat/galvanostat. The galvanostatic cycling of the all working electrodes was performed in the 2.1-0.003 V potential range *vs* Li/Li+ at a constant current density of 37.2 mA g^{-1} (C/10) for 50 cycles, or variable (93 mA g^{-1}, 186 mA g^{-1}, 372 mA g^{-1} and 744 mA g^{-1}, i.e. C/4, C/2, 1C, and 2C rates) 10 cycles at each current density, starting and finishing at the lowest one).

3. Results and discussion

3.1. Li+ ion intercalation/de-intercalation mechanism

The potential *vs* Li/Li+ against discharge-charge capacity plots (potential profiles) of the graphitized BCNFs are typical of graphite-