Expanded graphitic materials prepared from micro- and nanometric precursors as anodes for sodium-ion batteries

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ABSTRACT

A series of expanded graphitic materials are prepared from two different precursors: micrometric synthetic graphite and graphitized carbon nanofibers, and tested as anodes for sodium-ion batteries. The materials preparation involves the oxidation of the precursors followed by partial thermal reduction. Overall, the expanded synthetic graphite materials show better electrochemical performance as anode than the expanded graphite nanofibers, providing higher specific capacity, leading to lower capacity losses in the first discharge-charge cycle and exhibiting outstanding cycling stability. Specific capacities of $\sim$150 mA h g^{-1} at 37 mA g^{-1} and $\sim$110 mA h g^{-1} at 100 mA g^{-1} are attained, and up to 50% of the initial capacity at 19 mA g^{-1} is kept at 372 mA g^{-1}. Unexpectedly, higher capacity losses are measured for the nanostructured electrodes by progressively increasing the current density. These differences are attributed to the lower surface area and porosity of expanded synthetic graphite materials which favors the formation of thinner and more stable SEI, thus reducing the electrode resistance and enhancing the accessibility of Na$^+$ ions to surface oxygen-containing functional groups with the consequent increase of the surface capacity which was found to be the main contribution to the total specific capacity.

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1. Introduction

Since their introduction in the market in the early 1990s, rechargeable lithium-ion batteries (LIBs) have been the batteries of choice for portable electronic devices (cell phones, tablets, laptops, etc.). LIBs are also being used for other applications, such as powering electric vehicles, or in stationary large scale electrical energy storage (EES) systems from renewable energy resources (e.g., wind turbines or solar cells). However, among other considerations, the scarcity of lithium in Earth's crust (only 20 ppm) [1], together with the uneven distribution of lithium resources (mainly found in South America) and the increasing cost of lithium minerals ($\sim$\$5000/ton of lithium carbonate in 2010) [2] as a consequence of the growing demand have made the scientific community turn their attention to the development of sodium-ion batteries (SIBs), as shown by an exponential increase in the number of research articles on this topic since 2010 [1].

SIBs were initially studied alongside LIBs in the 1970s and 1980s [3,4], but afterwards they were overshadowed for a long time by the commercial success of their LIBs counterparts, with higher energy density. However, the natural abundance resources (4th

most widely abundant element on earth) and low cost (\$135–165/ton of mineral trona, from which sodium carbonate is produced) of sodium [2] as compared with lithium have made these batteries an attractive alternative to LIBs, particularly for their application in systems such as EES in which the cost is the overriding issue as they are made up of a great number of batteries, whereas the energy density at the battery unit level is not a critical factor.

Recent research on SIBs has benefited from the maturity reached after 30 years of R&D on LIBs. Thus, some of the cathodic materials investigated are analogous to those utilized in LIBs, only replacing lithium by sodium in the corresponding compound, these including layered oxides, phosphates, pyrophosphates, or fluorophosphates of transition metals, with promising results in some instances [1,2,5–10]. Similarly, the electrolyte formulations tested for these batteries consist mainly of sodium salts (NaPF$_6$, NaClO$_4$) dissolved in organic carbonates [11], which are also analogous to those employed in LIBs.

In contrast, development in the field of anodic materials for SIBs has been somewhat more limited, especially regarding carbon-based materials [12,13], since intercalation of Na$^+$ ions is practically hampered in graphite, anode of choice in most commercial LIBs. For example, intercalation compounds of the formula NaC$_{64}$ were obtained in low current density experiments for electrochemical intercalation of Na$^+$ in graphite [14], amounting to a reversible capacity $\sim$35 mA h g^{-1}, which contrasts with the stage-I graphite

intercalation compound, LiC_6, attained for Li^+ ions (theoretical capacity of 372 mA h g^{-1}). This limitation is partly due to the ionic radius of Na^+, which is ~0.3 Å larger than Li^+, as well as the stressed induced in the graphite structure when Na^+ ions are intercalated [15]. Interestingly, this has been circumvented in part in recent studies by the use of ether-based electrolyte systems allowing the co-intercalation of Na^+ ions with solvent molecules between the graphene layers, thus moderately increasing the reversible capacity delivered by graphite-based electrodes (100–150 mA h g^{-1}), as well as providing excellent rate capability [16–18].

However, most of the studies on carbon-based materials as anodes for SIBs have been focused on those with mean interlayer distances >0.37 nm, the minimum value required for Na^+ insertion in graphite-like structures according to theoretical calculations [19]. Thus, different carbon materials with diverse structures (micro- and nanostructures) and varied morphologies, usually with a certain degree of porosity and low-ordered structure consisting of few-layer graphite nanocrystallites, have been investigated for this application [12]. Among them, hard carbons are arguably the most promising candidates thus far [20–35], being able to deliver reversible capacities >300 mA h g^{-1} at low-to-moderate current rates with remarkable stability along cycling, although some aspects need to be improved for their implementation as anodes for SIBs, such as the relatively low coulombic efficiency in the first cycle, which is related to the high surface area and porosity of these materials, or their modest rate performance. The turbostratic structure of hard carbons, consisting in few-layer-stacked graphite nanocrystallites with high interlayer distances (0.37–0.40 nm), together with their inherent porosity (i.e. nanopores and nanovoids formed between different turbostratic domains) account for their dual mechanism of interaction with Na^+ ions: (i) reversible insertion of Na^+ in the turbostratic domains, which usually occurs in the potential range 1.0–0.2 V vs Na/ Na^+ resulting in sloping potential vs capacity profiles; (ii) Na^+ filling of nanopores and nanovoids in the structure, in a process similar to adsorption, giving rise to plateaus below 0.2 V vs Na/Na$^+$ in the same profiles [34]. From both mechanisms, the former would be preferable since pore-filling occurs at very low potential and may be accompanied by sodium plating which could lead to battery failure upon cycling due to electrical shorting. In fact, other carbon materials, such as carbon nanofibers [36] or reduced graphene oxides [37,38], showed no plateaus below 0.2 V indicating that their specific capacity was mainly due to Na^+ insertion into the graphene layers. However, very low coulombic efficiencies in the first cycle were calculated for these materials due to their large surface areas, making them impractical as potential anodes for commercial SIBs.

From the latter studies it can be concluded that an ideal carbon material for this application should have a layered structure with a long-range order, high interlayer distances and low porosity and surface area. In this regard, Wen et al. [39] prepared an expanded graphite (EG) through a facile synthetic route, involving the oxidation of a commercial graphite followed by a thermal treatment at 600 °C. This material had a relatively low surface area (~30 m^2 g^{-1}), a mean interlayer distance ~0.43 nm and was able to deliver high reversible capacities (~300 mA h g^{-1}) at low current densities, in the order of those delivered by hard carbons, with the advantage that most of this capacity was due to Na^+ intercalation/deintercalation processes (i.e., short sloping plateau below 0.2 V in the potential profiles). However, rate capability tests revealed a modest performance at high current densities, which is most likely attributed to the micrometric size of this material, hampering Na^+ ion diffusion within its turbostratic structure.

With these precedents in mind, in this paper the electro-chemical performance as anode for SIBs of novel expanded graphite nanofibers materials (EGNFs) is investigated by means of galvanostatic cycling at constant and variable (from 18.2 to high 372 mA g^{-1}) current density. The use of these expanded nanomaterials, prepared for the first time in our laboratory from graphitized carbon nanofibers (GNFs), should improve, a priori, the battery rate performance since they would allow faster insertion/de-insertion processes by reducing the diffusion length of Na^+ ions. In addition, expanded synthetic graphite materials (ESGs) obtained from micrometric synthetic graphite (SG) were also studied. Both types of expanded graphitic materials (EGs) were prepared by a two-step method involving oxidation of the graphitic material precursor, followed by thermal treatment of the graphite oxides (GOs). The anodic behavior of the different nano and micro EGs materials are discussed in terms of the battery reversible capacity, irreversible capacity in the first cycle, capacity retention and cycle efficiency by considering the influence of composition, graphitic structure, surface area and porosity. The mechanism of interaction of Na^+ ions with the EGs was also analyzed through cyclic voltammetry experiments at different sweep rates.

2. Experimental

2.1. Materials: source and preparation

The expanded graphitic materials (EGs) were prepared from two precursors: a synthetic micrometric graphite (SG), Timrex SLP50, from TIMCAL (www.timcal.com) which, according to the supplier, is a highly pure graphite (ash content <0.10 wt.%) with a perfect crystalline structure (interplanar distance, d_{002}, 0.3354–0.3356 nm, crystallite size L_c >250 nm) and a *Potato@Shape* particle morphology that is commercialized as active material for negative electrodes of lithium-ion batteries, and (commercial carbon nanofibers, PR-24-XT-PS, supplied by Pyrograf Products Inc. (http://pyrografproducts.com), that were subjected to a graphitization thermal treatment at 2800 °C (GNFs) [40], with d_{002} ~0.3389 nm and L_c ~15 nm.

The preparation of the EGs, namely expanded synthetic graphite (ESGs) or expanded graphite nanofibers (EGNFs), was carried out by a two-step process: (1) oxidation of the SG and GNFs precursors through a slightly-modified Hummers method [41] to obtain the corresponding oxides (SGO and GNFO), especially so in the case of GNFO, which was based on the oxidation of related carbon nanofibers and nanotubes in the literature [42–47] and (2) thermal treatment at three different temperatures (300, 600 and 900 °C) to partially reduce the oxides.

In a typical experiment to prepare SGO, $NaNO_3$ (1.5 g) was dissolved in H_2SO_4 (69 mL). Then, 3 g of SG were added to the solution and the suspension thus formed was vigorously stirred for 1 h at room temperature. Afterwards, $KMnO_4$ (9 g) was slowly added to the suspension, keeping the temperature below 20 °C with a water/ice bath. After heating at 35 °C for 1 h, the suspension color changed from black to dark brown and distilled water (200 mL) was then slowly added, keeping the temperature <98 °C. Once the addition was completed, the suspension was further stirred for 30 min at 98 °C, during which time the suspension color changed again from dark brown to light brown. Then, after leaving the reaction mixture cool down to room temperature, distilled water (140 mL) and H_2O_2 (30 wt.%, 30 mL) were added, successive-ly, and the suspension was left standing overnight to decant. After removing the supernatant liquid, the remaining brown slurry was washed with distilled water, the suspension was then centrifuged (4000 rpm, 30 min), decanting the supernatant liquid afterwards. This procedure was repeated several times until the supernatant reached the pH of distilled water (pH ~5–6). The aqueous slurry thus obtained was dried overnight in an oven at 60 °C to obtain a dark brown film which was ball-milled for the minimum amount of time required to obtain SGO as an homogeneous powdery dark brown solid.