Journal of Power Sources 279 (2015) 581–592

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Hierarchical self-assembled structures based on nitrogen-doped carbon nanotubes as advanced negative electrodes for Li-ion batteries and 3D microbatteries

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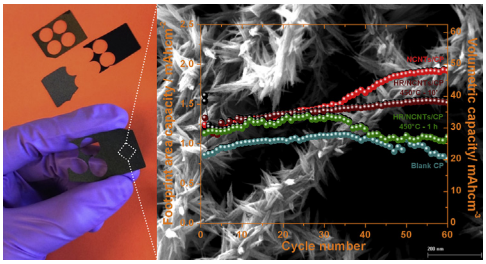
HIGHLIGHTS

- Hierarchical self-assembled structures with unique ‘tree-like’ morphology and functionalities are grown on carbon paper.
- The defective walls of N-doped CNTs provide favorable sites to grow hematite nanorods.
- Increasing Li storage, excellent coulombic and cycle efficiencies are obtained by incorporating N-doped CNTs.
- A thorough electrochemical analysis of the resulting hierarchical structures has been performed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 October 2014
Received in revised form
3 December 2014
Accepted 6 January 2015
Available online 7 January 2015

Keywords:
Li-ion microbatteries
Nitrogen-doped carbon nanotubes
Hematite
Self-assembly
3D negative electrodes
Carbon paper

ABSTRACT

Hierarchical structures based on carbon paper and multi-walled nitrogen-doped carbon nanotubes were fabricated and subsequently decorated with hematite nanorods to obtain advanced 3D architectures for Li-ion battery negative electrodes. The carbon paper provides a versatile metal-free 3D current collector ensuring a good electrical contact of the active materials to its carbon fiber network. Firstly, the nitrogen-doped carbon nanotubes onto the carbon paper were studied and a high footprint area capacity of 2.1 mAh cm^{-2} at 0.1 mA cm^{-2} was obtained. The Li can be stored in the inter-wall regions of the nanotubes, mediated by the defects formed on their walls by the nitrogen atoms. Secondly, the incorporation of hematite nanorods raised the footprint area capacity to 2.25 mAh cm^{-2} at 0.1 mA cm^{-2}. However, the repeated conversion/de-conversion of Fe_2O_3 limited both coulombic and energy efficiencies for these electrodes, which did not perform as well as those including only the N-doped carbon nanotubes at higher current densities. Thirdly, long-cycling tests showed the robust Li insertion mechanism in these N-doped carbonaceous structures, which yielded an unmatched footprint area capacity

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http://dx.doi.org/10.1016/j.jpowsour.2015.01.036

enhancement up to 1.95 mAh cm^{-2} after 60 cycles at 0.3 mA cm^{-2} and an overall capacity of 204 mAh g^{-1} referred to the mass of the entire electrode.

1. Introduction

Li-ion batteries (LIBs) currently dominate the market of portable electronics and their success has been related to their high energy density and versatility. However, these batteries are challenged in applications requiring increasing levels for both energy and power densities simultaneously, because such condition unavoidably creates a bottleneck [1–4] in conventional laminated electrodes, as well as in thin-film cells.

The use of nanostructures is generally regarded as a viable approach to reduce the path lengths of the charge carriers, while increasing the surface area for the active materials. Although this has a positive impact on the power density, because it improves the reaction kinetics and facilitates the uptake and removal of Li$^+$ ions and electrons, the energy density of nanomaterials remains inherently limited, due to their low tap density [5,6]. Moreover, the surface area enhancement due to the increased ratio between ‘bulk’ and ‘surface’ atoms in nanomaterials often can cause stability problems at the interfaces triggering side reactions [6]. The advantages deriving from the use of nanostructures are in most of the cases spoiled by their difficult or poor assembly into suitable electrodes [7]. In particular, agglomeration is one of the major problems when dispersing and stabilizing nanostructures, due to their high surface energy. In this respect, the idea of a three-dimensional (3D) electrode architecture is attractive, because the individual active nanostructures are directly wired to an extensive electrical network and all the ancillary materials (*i.e.* binders and conductive additives) can be avoided [8]. This raises the energy density of the entire electrode assembly, while retaining the beneficial characteristics of the nanostructured materials and their extended interfaces. 3D electrodes have thus the potential to address the main issues of conventional planar configurations, provided that a suitable matching of the materials ensures a good adhesion between the conductive network and the active component(s), without negating porosity and a quick access to both Li^+ and e^- through the entire structure [3,9]. These characteristics are crucial, especially if miniaturizing the entire battery would impose further limitations on the available space for its various components, which would need to be downscaled as well [2,9].

Recently, multi-walled (MW) nitrogen-doped carbon nanotubes (NCNTs) have attracted attention as an alternative material to graphite for negative electrodes, due to their unique Li storage properties, which significantly differ from those of other similar CNTs [10,11]. Apart from their outstanding electrical and mechanical properties, chemical stability, high aspect ratio and extended surface area, the presence of nitrogen atoms induces the formation of extrinsic defects that act as preferential adsorption sites for Li$^+$ ions, thus increasing the capacity [11]. This effect acquires a new dimension in NCNTs, because the Li$^+$ ions are also able to penetrate the defective tube walls and can be stored progressively in the inter-wall regions [11]. The space separating the coaxial tubular structures becomes thus available for Li insertion, enabling the use of their inner interfacial areas, which previously were not accessible. A high concentration of nitrogen doping in CNTs has been shown to positively affect both the reversible capacity and the rate capability [10] for the corresponding electrodes, although other studies show that also low levels of nitrogen doping can enhance the electrochemical activity of CNTs [12]. Theoretical studies of single-walled carbon nanotubes indicate that nitrogen doping should narrow the actual energy band gap for the fraction of semiconductor tubes, while causing electron backscattering for those having a metallic character [13–15]. A recent study shows also that diverse types of nitrogen defects may alter the electronic properties differently [16]. For MW-NCNTs, the presence of nitrogen enhances both the conductivity and the reactivity of the resulting CNTs [17–19], while the nitrogen defects create sites that can interact better with metallic nanoparticles [20,21]. Accordingly, MW-NCNTs could be used as a robust ‘reactive scaffolding’ to improve the electrochemical properties of other nanostructured materials such as metal oxides, which could grant access to even higher capacities, despite their typical limitations of poor conductivity and cycleability in conventional electrode structures. In particular, a material featuring multi-electron transfer reactions such as iron oxide (e.g. hematite) would be one of the best candidates to test the validity of such approach. Iron oxide undergoes a characteristic conversion reaction at low voltage *vs.* Li$^+$/Li, which involves the formation of Fe nanoparticles embedded in a Li_2O matrix following the reversible process indicated below [22]:

$$Fe_2O_3 + 6Li^+ + 6e^- \leftrightarrow 3Li_2O + 2Fe \qquad (1)$$

This particular electrochemical mechanism generates a theoretical specific capacity of 1007 mAh g^{-1}, which is one of the highest among transition metal oxides (TMOs) undergoing similar reactions. Nevertheless, Fe_2O_3 presents a series of problems, namely; *i.* scarce electronic conductivity, *ii.* agglomeration for its nanoparticulated forms, *iii.* significant volume variation upon lithiation/delithiation (*i.e.* ≈93%), *iv.* poor Coulombic efficiency in the first cycle, *v.* pronounced voltage hysteresis between discharge and charge (*i.e.* low energy efficiency) and, ultimately, *vi.* limited capacity retention. These issues have hindered its practical applications in advanced batteries [23,24]. Different strategies have been applied to partly address these problems, which are common to most of the convertible TMOs. Among others, hybrid nanomaterials [25] combining iron oxide (and other TMOs) with a conductive matrix, such as graphene [26] or CNTs [27] have been utilized to overcome agglomeration problems and buffer the volume changes. In fact, hematite (α-Fe_2O_3) can beneficiate from a direct contact with a conductive support providing a favorable pathway for electron transfer, thus addressing its short carrier diffusion length [28] (a few nanometers). This approach helps reducing the interfacial resistance, thereby improving the capacity retention at high cycling rates [29,30].

One of the main advantages of nanotubes as a conductive network is that they intrinsically offer a high ‘surface to volume’ ratio, and, since they are made of carbon, they possess a very low density. Still, the main difficulty with hybrid nanomaterials remains, e.g. achieving a solid attachment of the conductive network to the current collector without using any binder or additives, while retaining a superior electrode architecture and integration of each component [31].

With these ideas in mind, the present study focuses on understanding the role of NCNTs to advance the production of 3D negative electrodes for Li-ion batteries, while including additional