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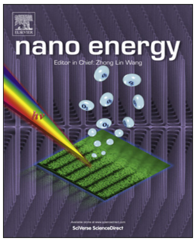

RAPID COMMUNICATION

Hierarchically structured nanocarbon electrodes for flexible solid lithium batteries

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Abstract
The ever increasing demand for storage of electrical energy in portable electronic devices and electric vehicles is driving technological improvements in rechargeable batteries. Lithium (Li) batteries have many advantages over other rechargeable battery technologies, including high specific energy and energy density, operation over a wide range of temperatures (−40 to 70 °C) and a low self-discharge rate, which translates into a long shelf-life (~10 years) [1]. However, upon release of the first generation of rechargeable Li batteries, explosions related to the shorting of the circuit through Li dendrites bridging the anode and cathode were observed. As a result, Li metal batteries today are generally relegated to non-rechargeable primary battery applications, because the dendritic growth of Li is associated with the charging and discharging process. However, there still remain significant advantages in realizing rechargeable secondary batteries based on Li metal anodes because they possess superior electrical conductivity, higher specific energy and lower heat generation due to lower internal resistance. One of the most practical solutions is to use a solid polymer electrolyte to act as a physical barrier against dendrite growth. This may enable the use of Li metal once again in rechargeable secondary batteries [2]. Here we report a flexible and solid Li battery using a polymer electrolyte with a hierarchical and highly porous nanocarbon electrode comprising aligned multiwalled carbon

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Abbreviations: CNT, carbon nanotube; CNH, carbon nanohorn; TEM, transmission electron microscope; STEM, scanning transmission electron microscope; SEI, solid electrolyte interface

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nanotubes (CNTs) and carbon nanohorns (CNHs). Electrodes with high specific surface area are realized through the combination of CNHs with CNTs and provide a significant performance enhancement to the solid Li battery performance.

Introduction

Carbon, usually in the form of graphite, is a readily available and cost effective material commonly used as the negative electrode in Li-ion battery structures. The stability of the sp^2 covalent bonds and ability to weakly bind Li gives rise to large storage capacities at a high Li chemical potential. As far as carbon is concerned, graphite is particularly interesting owing to its high electronic (in-plane) conductivity resulting from the delocalized π-bonds. Li ions intercalate between the graphite layers, and theoretically, one Li atom requires six carbon atoms to intercalate, resulting in a theoretical capacity of 372 mAh/g of graphite. However, practical limits in performance have been reached for natural graphite electrodes.

Necessary characteristics for a material to be attractive as an anode material in lithium-based batteries are: high Li capacity, high chemical potential of the Li of the lithiated compound, fast Li insertion/extraction kinetics and small volume changes during Li insertion/extraction [3].

The development of nanostructured graphitic carbons, e.g. CNTs [4], permits some control over pore size and accessibility, opening the prospect of designing electrodes with higher reversible capacity as well as superior cycling stability. High electronic conductivity is important in bringing the electronic carriers from the current collector to the Li atom(ion) as rapidly as possible, as is a good diffusion rate of Li into the electrode, which permits a higher utilization of the electrode. These parameters may be enhanced by electrode design, for instance by orienting the CNTs vertically with a direct connection to the substrate, which would enable the extraction of quick bursts of energy (high power), by reducing the overall equivalent series resistance (ESR) of the cell.

While CNTs are a form of nanoscale tubular graphene sheet, CNHs are formed from graphene sheets in horn-like shapes with open ends [5]. They can be viewed as being formed from the crushing or origami-like contortion of a graphene sheet. CNHs can be prepared with high purity as a low-cost raw material in a process which is easily scalable to produce large volumes. The advantage of using CNHs in energy storage devices lies not only in their large surface area (1000–2000 m^2/g) but also in the easy permeation of gases and liquids [6,7] through their agglomerates.

In previous reports, aligned CNT forest electrodes were often fabricated in a multistep and usually complex manner, including peeling-off grown CNTs from the growth substrate and post sputtering of charge-collecting metal layers [8]. This is due to the complexity of growing CNT arrays onto flexible metallic substrates, which is common for battery fabrication and stable against corrosion. The cost of volume production of CNTs and the complexity of the fabrication processes have been the barriers for commercial adoption of these synthetic nanostructured carbon electrodes to date.

The electrolyte, the medium which transports charged ions between anode and cathode, typically consists of an organic solvent with a Li salt. Although a solid ion transporting medium would be ideal, polymer electrolytes to date have suffered from a poor room temperature ionic conductivity ($\sim 10^{-4}$ S/cm vs. $\sim 10^{-2}$ S/cm for liquid electrolytes) [9]. The Li-polymer battery, first released by Sony, achieved a compromise; it used a “gel” electrolyte composed of a polymer matrix swollen by a high proportion of a solvent for the lithium salt. The gel had a reported conductivity of 3×10^{-3} S/cm at 25 °C [10]. This structure benefits from acceptable ionic conductivity as well as structural stability.

Here we report a solid, yet flexible Li battery based on the hierarchical combination of CNTs and CNHs as the cathode and a solid poly(ethylene glycol) borate ester as the electrolyte. Vertically-aligned CNTs are synthesized directly on flexible charge collectors (e.g. aluminum foil) and used as scaffolds for CNHs. The use of these carbon electrodes with a hierarchy of nanostructures leads to a significant improvement in the battery performance. The combination of a polymer solid electrolyte with the nanostructured electrode provides further advantages of flexibility and safety in a solid lithium anode battery.

Materials and methods

A custom CVD method has been developed for the low temperature (520 °C) synthesis of packed vertically aligned CNT arrays. Multiwalled CNTs were grown directly on the charge collecting substrate, typically regular 10–15 μm thick aluminum (Al) foil. This provides an advantage to *ex-situ* chemical vapor deposition (CVD) growth and post processing (e.g. making mixtures of carbon with poly(vinylidine fluoride) etc.) [11]. Commercially available, 10–15 μm-thick Al foil was cut and cleaned using acetone and isopropanol, followed by a deionized (DI) water rinse and drying in nitrogen. A 10–15 nm-thick iron film sputtered onto the cleaned foils acted as the catalyst layer for the CNT growth. Multiwalled CNTs were grown using an Aixtron Nanoinstruments Plasma Enhanced Chemical Vapor Deposition system. Briefly, growth was carried out in a quartz vacuum chamber on a resistively heated graphite stage. Growth temperature was controlled by a thermocouple attached to the surface of the graphite stage. Following catalyst deposition, samples were placed on the graphite stage in the quartz chamber, which was then evacuated to 10^{-2} mbar. After that, samples were heated up to 480 °C with ammonia gas (NH$_3$, 200 sccm flow rate) and annealed at this temperature for 2 min. Catalytic nanoparticles were found on the foil after annealing, essential for low temperature growth. After annealing, the graphite stage temperature was ramped to 520 °C. NH$_3$ was turned off and acetylene (C$_2$H$_2$) was supplied (200 sccm flow rate) as the carbon feedstock for the CNT growth. The chamber pressure

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