Interconnected foams of helical carbon nanofibers grown with ultrahigh yield for high capacity sodium ion battery anodes

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Abstract

Here we demonstrate the growth of three-dimensional foams of defect-containing helical carbon nanofibers for application in efficient sodium ion battery anodes. Using pretreated Ni nanowire templates, over 3500% growth yield is observed for helical CNF foam materials, which can be directly incorporated into a sodium-ion battery anode. Our work demonstrates that the tortuous bends in helical CNFs provide a balance of nanodomains and defect sites that are responsible for high performance sodium storage. This includes sodium storage capacity exceeding 280 mAh/g at moderate rates of 100 mA/g with stable cycling performance over 200 cycles. Raman spectroscopic analysis during sodiation sheds insight into storage behavior of this material that confirms defect and nanopore mediated storage over the formation of an ordered intercalation compound. This work presents an intersection between the large-scale controlled growth science of carbon nanostructures and carbon materials optimized for efficient sodium storage applications.

Key Words: carbon nanofibers, chemical vapor deposition, sodium ion batteries

1. Introduction

As emerging technological areas such as electric vehicles and robotics are evolving to incorporate portable and rechargeable energy storage systems, the demands on cost, safety, and performance of battery technology are rapidly increasing. Sodium-ion batteries (SIBs) stand out as a promising platform to replace lithium-ion batteries due to the significantly increased earth abundance of sodium compared to lithium that can enable battery technology to penetrate grid-scale storage applications. However, numerous challenges in transitioning from lithium-ion to sodium-ion storage systems have been isolated [1, 2]. Chiefly, as the radius of sodium ions is nearly 1.3X larger than that of lithium ions, simply using the same host electrode materials (crystalline carbons and metal oxides) leads to poor performance for SIBs. Studies have shown the maximum sodium capacity of graphitized carbon anodes to be < 35 mAh/g, which is over 10X lower than that possible with the same materials using lithium ions [3].

Despite a number of studies centered on the sodium storage capability of carbons, the sodium storage mechanism in these materials remains controversial and a dynamic area of ongoing research. Early studies highlighted a house of cards type model consisting of two key storage modes for sodium in carbons: (1) storage of ions in between graphene layers which corresponds to the sloping voltage profile during sodiation; (2) ions filling the micro/nanopores (“pore-filling”) in the carbons at lower potentials [4-7]. More recent experiments have highlighted the sodium storage behavior of a series of pseudographite materials derived from sustainable sources, such as banana peels, emphasizing the critical optimization of porous nanodomains, defects, and intercalation for sodium storage [8-10]. These studies propose that the nanodomains in the carbon are critical to enable high

capacity filling of the Na^+ , which is correlated with the higher voltage component of the insertion curve. Lotfabd *et al.* further study the storage mechanism in the absence of reversible pore filling, observing a dilated interlayer spacing associated with sodium intercalation [10]. On the other hand, Bommier *et al.* carefully study defect-controlled hard carbons and conclude the (higher voltage) sloping voltage profile during sodium insertion is correlated to the defect content of the material, and similarly propose a surface reaction that leads to pore-filling of turbostratic nanodomains at lower voltages [11]. Alternatively, other routes have highlighted the mechanism for solvent cointercalation [12, 13] of Na^+ species in carbon materials that enables extraordinary cycling and rate capability while still maintaining up to 150 mAh/g sodium storage capacities, as recently demonstrated for few-layered graphene [14]. Whereas researchers have reported a variety of carbon nanomaterials, usually based from defect-containing and/or hard carbons, to have attractive sodium storage properties [15-23], the engineering of carbon nanostructures to enable optimize sodium ion storage properties remains an area ripe for discovery and understanding. Further, a comprehensive understanding of sodium storage in carbons, which is likely to be dependent on the chemistry and physical characteristics of the carbons, remains elusive.

On another front, the growth, assembly, and energy applications of carbon nanomaterials in three-dimensional self-organized structures has been primarily centered on the science and applications of small diameter and high quality carbon nanotubes (CNTs) due to improved properties of these materials over their more defective counterparts [24, 25]. CNT-based interconnected solids or foams with elbows and defect-containing morphologies that stray from linear CNTs have been an emerging focus of

recent research efforts [26-28]. The ability to engineer the defect content and structural properties of CNTs and carbon nanofibers (CNFs) in as-grown solids represents a research area that can extend the versatility of 3D foam structures of carbon nanomaterials to applications such as oil recovery, sensing, and other energy applications. Notably, based on recent advances in the understanding of sodium ion batteries [8, 11], such architectures should be ideally suited for this application.

Here we demonstrate the ability to pretreat nanoscale nickel materials using electrochemical oxidation to activate ultrahigh yield growth performance of high defect-content helical CNF materials. The CNF material can be directly incorporated as an anode into a sodium ion battery, exhibiting excellent sodium ion storage capacity and cycling capability attributed to a combination of defects and nanoporous regions in the carbons. Our efforts further use Raman spectroscopy to highlight the mechanistic benefit of the high-defect content tortuous bends in helical CNF materials to enable stable, high capacity anode cycling performance.

2. Experimental

2.1 Preparation of CNF growth substrate

To grow helical CNF foams, commercially purchased Ni nanowires (Fig. 1a) were soaked in 0.1 M NaOH (Sigma Aldrich) overnight (~18 h) and rinsed with deionized water (18 M Ω , obtained from a Millipore Milli-Q system). Electrochemical oxidation process [29, 30] of pre-soaked Ni nanofoam was performed in deionized water initially under 30 V, using two same pieces of Ni nanofoams as both counter and working electrode. 0.1 M NaOH was added dropwise and stirred mildly until the current reached

to ~ 5 mA. Then DC potential was maintained for 30 min. After oxidation, the nanofoams were rinsed with deionized water until neutral pH was achieved. The working electrode was used for further characterization and as a high yield substrate for CNF growth. Fig. 1b shows a SEM image of a representative electrochemically textured Ni material used as a precursor to grow helical CNFs. Notably, whereas our efforts build upon the use of Ni nanowires to optimize CNF yield, we observe this process to be universally applicable to any Ni material morphology to produce an oxidized and textured surface.

Fig. 1. SEM images of (a) network of untreated Ni nanowires and (b) electrochemically oxidized network of Ni nanowires with a spiky surface that enables activation for high-yield helical CNF growth.

2.2 Helical CNF growth

A few mg (less than 1 mg) of the pretreated Ni nanowire material was placed into an alumina crucible, and placed into the central region of a chemical vapor deposition (CVD) system comprising a Lindberg Blue 1" tube furnace. To assess the ability for the oxidized Ni nanowires to maintain their textured surface morphology under reduction, we first

analyzed this point. The furnace was first ramped up to 500 °C under 400 sccm Ar. Then 200 sccm of H₂ were introduced and kept for 20 minutes for reduction of oxidized and textured surface of the pretreated Ni nanowires. Then H₂ was turned off and the furnace was cooled down to room temperature under Ar flow. To grow the helical CNFs, the growth process is performed by using the same set-up in Lindberg Blue 1” tube furnace. The furnace was ramped up to 500 °C again under 100 sccm Ar. Then 50 sccm H₂ and 2.5 sccm acetylene was introduced for 30 minutes for helical CNF growth. After growth process finished, H₂ and acetylene were turned off and the sample was cooled down to room temperature under Ar. As a control material, the same process was carried out on a Ni nanowire material with no electrochemical texturing, and hence a smooth surface morphology.

2.3 Material characterization and battery measurements

Scanning electron microscopy (SEM) imaging of the Ni nanowires, electrochemically oxidized Ni nanowires, and helical CNF materials was performed using a Zeiss Merlin Scanning Electron Microscope. Transmission electron microscopy (TEM) characterizations of CNFs were performed by using an FEI Osiris TEM. Raman spectroscopy of carbon nanofibers was conducted on a Renishaw inVia MicroRaman system with 785 nm laser excitation. *Ex-situ* Raman analysis was achieved by using a homemade air tight system with a glass slide on top as observation window.

To produce battery electrodes, the CNFs were mixed with conductive carbon black (TIMCAL SUPER C45) and poly(vinylidene difluoride) (PVDF, Alfa Aesar) as binder with mass ratio 80:10:10. Then the mixed electrode materials were dissolved in N-methyl

pyrrolidinone (NMP) and sonicated for 1 h to form a slurry. The slurry was drop-casted onto a stainless steel surface and dried in vacuum oven at 100 °C overnight. All electrochemical measurements were performed in CR 2032 type coin cells assembled in Ar-filled glove box. Sodium metal (Sigma Aldrich) was used as counter electrode. 1 M NaPF₆ (Strem, 99%) in ethylene carbonate (EC)/diethyl carbonate (DEC) (Sigma Aldrich, 99%/ $>99\%$) with volume ratio 4:6 was used as electrolyte. A Whatman grade GF/F glass fiber microfiber filter (Sigma Aldrich) was used as separator. Cyclic voltammetry (CV) measurements were performed on a Metrohm Autolab Multichannel analyzer from 0.01-3 V at a scan rate of 0.1 mV/s. Galvanostatic charge/discharge was performed on an MTI 8 channel battery analyzer between 0.01-3 V with a current density of 100 mA/g. Various current densities of 50, 100, 200, 500, and 1000 mA/g were applied for rate study.

3. Results and Discussion

The nucleation and growth of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) is correlated to the formation of active nanostructured particles of catalytic metal on surfaces that support growth. Whereas numerous and broad efforts have been carried out to understand the types of catalyst materials and support layers to sustain catalytic growth of carbon nanostructures [24], the effect of surface morphology – especially with extreme nanoscale texturing, on such growth processes is not well understood. In this effort, we studied the growth of carbon nanostructures on electrochemically textured Ni nanostructures in order to explore the capability to directly grow an engineered carbon nanomaterial that can be incorporated as a sodium ion battery anode. Nanotextured Ni material used for helical CNF growth is shown in Fig. 1a. During electrochemical oxidation in water, the electric field applied to the Ni nanowires leads to nucleation and

growth of pyramidal oxide nanocrystals on the surface of the Ni, leading to a uniform distribution of surface spikes (Fig. 1b). Using such materials to grow carbon nanostructures is based on the premise that pretreatment of metal surfaces can be instrumental to enable or enhance catalytic activity from surface through mechanisms such as oxide surface reconstructions [31]. In this manner, we performed growth studies under conditions where the thermal reduction of the electrochemically pretreated “spiky” Ni nanowires maintains the spiky surface on a catalytic metal growth template (Supporting Information Fig. S1) that can hence impact the yield of catalytic growth.

To grow foams of helical CNFs, both the electrochemically textured and untreated Ni nanowire materials were used to compare the resulting growth performance. A key observation in our studies is that pretreated, oxidized Ni nanowires with spiky surface features lead to the growth of ultrahigh yield foams of carbon nanostructures. Whereas both the treated and untreated Ni materials lead to CNF growth, the size and mass of the CNF foam materials grown from the pretreated Ni templates are significantly greater than that observed from untreated Ni templates. As an example, with 0.48 mg spiky Ni nanostructures used in CVD growth, the resulting mass of bulk free-standing carbon foam composed of CNFs was 17.46 mg (3538 wt% increase). Similarly, with 0.83 mg untreated Ni materials in the same growth process, the mass of carbon foam was 13.49 mg (1525 wt% increase). The high yield of CNFs based on Ni template before and after CVD growth is visually shown in Fig. 2b and Fig. 2c. This trend was consistently observed in numerous experiments. Such increased yield with oxidative pretreatment has been observed with stainless steel and attributed to oxygen reconstruction on the surface to enhance growth yield [31]. In our case, whereas we anticipate growth occurs from Ni

Fig. 2. (a) Schematic illustration of the improved yield achieved from textured (pre-treated) Ni nanowire substrates. (b-c) Pictures of nanowires prior to growth (b) and after growth (c) from pretreated textured Ni surfaces. This leads to an evident high yield of a compact foam of helical CNF materials.

metal surfaces, the electrochemically-induced reorganization of metal into a textured morphology increases the total amount of catalytic metal exposed to C_2H_2 precursor at the onset of nucleation, leading to overall greater catalytic activity from the same total

mass of metal catalyst-containing materials. Specifically for battery applications, the ultrahigh yield of this process leads to a material that can be directly incorporated into a battery anode without need for further processing, as the carbon mass is significantly greater than that of the mass of the catalytic metals.

To characterize nanocarbon materials in the foams during the growth process, SEM and Raman spectroscopic analysis was performed (Fig. 3). Notably, both the electrochemically pretreated (spiky) and untreated Ni nanowires led to the catalytic growth of the same types of CNF materials based on SEM analysis and Raman spectroscopic characterization (Fig. 3a-b) indicating growth conditions and not substrate pretreatment led to the resulting helical CNF materials. Overall, a wide distribution of CNF diameters were observed in SEM, with the majority of CNFs (> 80%) exhibiting arms or helical architectures representative of a high defect concentration in the carbon material. Raman spectroscopy analysis (Fig. 3b) on foams grown from both pretreated Ni materials and untreated Ni materials indicates a similar intensity ratio and peak position of the D and G bands in both samples (*e.g.* $I_D/I_G \approx 1.6$), indicating a high defect content that is necessary for such arms and twists in the helical CNFs to form. A close-up view of a single representative helical CNF (Fig. 3c) indicates the tortuous arrangement of carbon with nanopores at the high defect-containing elbow areas that are well-suited for sodium storage. High magnification TEM analysis of the graphitic ordering (Fig. 3d) and the helical bends (Fig. 3e) confirms a turbostratic arrangement of carbon in the form of CNFs with pores and ridges at elbows and bends in the materials. Overall, based on previous discussion on the mechanistic foundation of sodium storage processes in carbon materials,

the high defect content of these materials combined with the accessible pores on the interior of the CNFs makes these materials ideally suited for Na-ion batteries.

Fig. 3. (a) Zoomed-out SEM image of as-grown CNFs showing fiber diameters and morphology. (b) Raman spectra from CNFs grown both from untreated Ni Nanowire materials and pretreated (oxidized) Ni nanowires. TEM images of (c) a single helical CNF, (d) CNF carbon material with small diameter features, and (e) 'elbow' area of helical CNF.

To study the performance of these materials in batteries, coin cells were produced with foam materials in half-cell configurations with a Na metal counter electrode. Galvanostatic charge/discharge measurements were used to explore the sodium ion storage properties of CNFs. Fig. 4a (solid lines) showed the 1st cycle charge/discharge

comparison of CNFs grown from both pretreated (high-yield) and untreated (low-yield) Ni nanostructures. For high-yield helical CNF foams, a high capacity of 1008 mAh/g upon initial discharge was measured with a reversible capacity of 283 mAh/g for the 2nd cycle (Fig. 4a; dotted lines). The large irreversible capacity in the 1st cycle is attributed to the solid-electrolyte interphase (SEI) formation [18] due to the irreversible decomposition of electrolyte on the first cycle [15] and irreversible Na absorption at defect sites [10]. Following the first cycle, the charge-discharge performance exhibits a high Coulombic efficiency indicating a stable SEI layer formed in the first cycle. A similar observation was made for the CNFs grown from untreated Ni nanofoams (low-yield), except the total magnitude of capacity is lower due to the greater percentage of dense Ni metal in the nanofoam anode. In both cases, the majority of the sodium storage capacity can be attributed to the higher voltage sloping region in the charge-discharge curves. This region has been previously correlated with irreversible capacity in pseudographite materials [10] and defect-induced storage in controlled studies of hard carbons [11]. To further analyze the details of sodium storage electrochemistry, cyclic voltammetry measurements were carried out on helical CNF foam materials following the initial SEI formation. In these cases, similar results to that observed in galvanostatic data is apparent, with a sodium insertion/extraction redox couple that occurs generally below 0.5 V vs. Na/Na⁺, with a sloping region below 1 V, and a strong contribution from the low-voltage insertion/extraction at lower voltages. Both materials show identical performance, except that the higher yield CNF foam leads to better specific storage capability due to a higher yield growth process. Notably, the origin of these electrochemical features remains a topic of controversy that has proven difficult to controllably establish likely due to the

different chemical and physical characteristics that carbon materials exhibit (*e.g.* defect density, crystallinity, nanodomain size and density, *etc.*) across separate studies. Recent work by Bommier *et al.* [11] proposes the high voltage sloping region to be correlated to the defect density of the carbons, and Lotfabd *et al.* [10] correlates this sloping region to irreversible capacity that is likely associated with defects. However, insertion at lower voltages has been correlated to underpotential (plating) deposition of metal into turbostratic nanodomains [11] or reversible intercalation into the carbons [10]. Across studies centered on different materials, researchers have observed a varying reversible capacity associated with these two distinct voltage ranges for sodium storage. Recent studies that demonstrate sodium storage exclusively in the higher voltage sloping region indicate cycling with no capacity fade measured over 600 cycles [32], which is improved compared to devices with a low voltage plateau. From our data, we observe two apparent characteristics associated with insertion. Between ~ 1 V to 0.3 V vs. Na/Na⁺, we observe a sloping profile that we associate with defect mediated storage that occurs at higher voltages due to the favorable energetics of sodium storage at defect sites. At lower voltages (< 0.3 V), we observe a distinct insertion characteristic attributed to underpotential deposition associated with filling of nanopores that arise in the tortuous bends observed in helical CNFs (Fig. 3).

Cycling performances of CNFs are shown in Fig. 4c. For helical CNFs grown with high yield (pretreated Ni nanowires) and cycled as batteries at 100 mA/g, Coulombic efficiency was higher than 95% after the 5th cycle and capacity retention ~ 98 % was maintained until 200 cycles (Supporting Information Fig. S2). A similar observation was made for helical CNFs grown on untreated Ni materials, except with a lower total

capacity during cycling consistent with other data. This implies that after stable SEI layer formation in these materials, the helical foams exhibit excellent cycling performance. Further, rate capability measurements were performed at rates between 50 mA/g and 1000 mA/g, with a moderate stable capacity above 120 mAh/g at the fastest rates, indicating good rate performance.

Fig. 4. (a) Charge/discharge profiles of the 1st (dotted lines) and 2nd (solid lines) cycle at rate of 100 mA/g, (b) CV profiles showing the reversible storage performance of helical CNF anodes (100 mV/s), (c) cycling performance and Coulombic efficiency of helical CNFs at 100 mA/g, and (d) rate capability from charge-discharge tests at rates from 50 – 1000 mA/g.

To better understand the mechanistic sodium storage behavior of helical CNF foams, Raman characterization was performed on cells in the absence of air exposure both before and after sodiation of the CNF materials. Prior to sodium insertion, the Raman modes of the helical CNFs match those shown in Fig. 3b, with a similar D and G band intensity representative of a significant presence of sp^3 defective carbon in the CNFs. After sodiation, the D band exhibits a blue shift to a peak center of $\sim 1315\text{ cm}^{-1}$ and G band red shifts to a peak center $\sim 1590\text{ cm}^{-1}$. There was no significant change in I_D to I_G ratio, indicating that sodiation does not lead to the notable formation of additional defect sites, but rather maintains the carbon coordination inherent to the pristine material. However, both the D and G bands exhibited peak broadening after sodiation. This similar behavior was observed in multiple subsequent tests. Similar qualitative peak shifting and broadening phenomena has been reported from *in-situ* Raman assessments of EMI^+ intercalation in activated carbon [33]. In this study, the D peak blue shift was explained as the disappearance of ring breathing modes at edges of crystalline domains, while the G peak red shift was explained through charge transfer. Notably, the peak shifts that are observed in our material are not generally consistent with that typically observed for both Li^+ and Na^+ intercalation in crystalline carbons [14, 34, 35], where ordered intercalation compounds evolve from dilute staging processes. Specifically, Raman modes of ordered stage 4 through stage 1 compounds in graphite materials are clearly distinguishable [34]. However, in contrast to this, our results for fully sodiated helical CNFs indicate only minor modification of the D and G band Raman signature that does not appear to reflect staging effects in a carbon intercalation compound (Fig. 5). This would imply that the sodium storage in the helical CNFs does not appear to form an ordered intercalation

Fig. 5. Raman analysis of helical CNFs before (black) and after (red) sodiation. The solid curves are Lorentzian fits. Data has been normalized to the D peak for clarity. Inset is a scheme highlighting one possible explanation for the observed shifts, noting this observation deviates from that expected from a highly ordered intercalation compound.

compound of $\text{Na}_x\text{C}_{1-x}$. This is in general agreement with a recent simulation study that emphasizes positive formation energy for high capacity sodium intercalation compounds in graphite indicating that, without some perturbation to the graphite lattice energetics, a high capacity sodium-graphite intercalation compound is thermodynamically prohibited [36]. However, Lotfabd *et al.* [10] describe an initial irreversible capacity associated with residual metal atoms maintaining positions at carbon defect sites that will provide local charge-transfer induced strain fields which could possibly assist in overcoming energetic barriers of intercalation into pristine graphite. Whereas our results do not elucidate the

local storage near or at defect sites, the high specific capacity (comparable to stage 1 NaC_8) and lack of an ordered staged compound is likely to indicate the role of the low-voltage pore filling in the storage mechanism of helical CNFs, as discussed by Bommier *et al.* [11]. We therefore interpret this asymmetric Raman response and broadening to be a result of mechanical stresses and charge transfer at the carbon-sodium interface associated with the insertion and extraction of sodium from the material. Based on previous Raman studies [37, 38] this response can be explained by local tensile stresses and charge transfer associated with sodium interfaces with carbon – either at defect sites or at filled pore sites. This leads to a system where capacities approaching ordered compounds such as LiC_6 can be achieved through a combination of defect sites that provide local storage and “on-ramps” to embedded pores, as well as micropore domains that facilitate local plating. Notably, this is also distinguished from co-intercalation [13] which does form ordered compounds containing Na^+ , carbons, and solvent molecules with an appreciable storage capacity. Further studies building upon pioneering techniques, such as the scotch tape method [39], can lead to direct assessments of the interplay between defects, pores, intercalation, and/or underpotential deposition processes that are likely strongly correlated to the physical and chemical properties of the carbon materials. However, in our work we emphasize that helical CNF materials provide an excellent template for high capacity sodium storage, and combined with the versatility of controlled growth processes, can enable insight into the controversial and diverse intercalation mechanisms observed so far in a series of different carbon materials.

Conclusion

In summary, we have demonstrated an approach to electrochemically pretreat Ni nanowire precursors to form textured growth surfaces that yield solid foams of helical CNFs with ultrahigh yield. These helical CNFs provide a combination of defect sites and nanoporous regions in the bends and arms which activates their function for optimized sodium storage. With ultrahigh yield growths, we demonstrate the ability to directly incorporate as-grown CNF foam materials as anodes in sodium ion batteries, with high reversible capacity exceeding 280 mAh/g and stable cycling performance for 200 cycles. We use Raman spectroscopy to assess the storage properties of this material, and highlight a mechanism of storage that is distinguished from conventional staging processes combining both pore filling and defect activated storage, in correlation with previous reports. This work provides a comprehensive connection between controlled, high-yield growth of carbon nanomaterials and direct incorporation of this material into sodium battery electrodes – an approach scalable to low-cost battery manufacturing processes.

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