Short communication

Carbon nanocolumn arrays prepared by pulsed laser deposition for lithium ion batteries

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ABSTRACT

Carbon nanocolumn arrays have been fabricated directly onto a titanium foil by a pulsed laser deposition (PLD) technique using graphite as a target. The sample has been characterized by scanning electron microscopy, high resolution transmission electron microscopy, selected area electron diffraction, and X-ray photoelectron spectroscope. The carbon nanocolumns with aspect ratio over 20:1 are composed of plenty of curved graphite sheets stacked parallel to the substrate. The initial discharge and charge capacities of these carbon nanocolumns are approximately 1060 and 670 mAh g^{-1}, respectively, at a rate of 0.1 A g^{-1}. A reversible capacity of approximately 315 mAh g^{-1} is still retained after 50 cycles. The good electrochemical performance and high aspect ratio suggest that the carbon nanocolumn arrays are promising microelectrode for three dimensional microbattery applications.

1. Introduction

There is increasing demand of energy storage devices with reduced size and high energy densities for applications in microelectronic devices, such as smart cards, sensors, electronic chips and implantable medical microdevices. Among the existing energy storage devices, thin film lithium ion microbatteries with merits of high energy densities, superior power densities and long cycle life are regarded as the most competitive energy sources for such applications [1,2]. Such lithium ion batteries are constructed by the deposition of cathode, electrolyte and anode solid films on a substrate sequentially by techniques, such as chemical vapor deposition (CVD), vacuum thermal vapor deposition (VD), RF sputtering (RFS), and RF magnetron sputtering (RFMS) [1–3]. However, the specific energy density of these thin film microbatteries is quite limited and large active area is necessary to achieve satisfactory capacity. Thus, 3D microbatteries based on well-aligned electrode arrays with high aspect ratio have been proposed to increase the energy density [4,5]. The key challenge in the fabrication of 3D microbatteries lies in the rational selection of appropriate electrode materials and the development of a feasible approach to make these electrode materials into 3D architectures with high aspect ratio.

Carbon materials have already been adopted as negative electrode in conventional lithium ion batteries due to their low cost, high stability and safety. In addition to graphite, a variety of carbonaceous materials [6,7], including mesocarbon microbeads (MCMB) [8], nanotubes [9,10], nanofibers [11], nanocages [12], microporous carbon [13], and mesoporous carbon [7,14] have been successfully prepared and evaluated as negative electrodes for lithium ion batteries. It is proposed that carbon nanostructures are good anode materials for lithium ion microbatteries. Recently, carbon microcolumn arrays fabricated through the pyrolysis of patterned photoresist in an inert atmosphere have been considered as a carbon microelectromechanical system (C-MEMS) for 3D microbatteries [15–17]. This 3D carbon electrode delivers a reversible capacity of approximately 220 mAh g^{-1}. Highly ordered carbon micro-net films (CMNFs), another 3D materials of C-MEMS, have also been prepared through patterning and pyrolyzing photoresist films [18]. These CMNFs are potential anode for 3D microbatteries. However, a multi-step procedure that involves spin-coating, UV illumination, and high temperature pyrolysis is required for the preparation of the carbon microcolumn arrays and micro-net films. Moreover, the energy densities of these carbon electrodes are limited. Thus, it is highly desirable to develop an approach to prepare carbon nanostructures with high aspect ratio for 3D microbatteries. Herein, a pulsed laser deposition (PLD) technique has been employed for the preparation of carbon nanocolumn arrays with high aspect ratio directly on a current collector, titanium foil at room temperature. The current collector with carbon column

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arrays can be used as an electrode for lithium ion batteries without further post-treatment. This PLD method obviously simplifies the preparation procedures of the carbon column arrays, and the electrode as well. The superior electrochemical performance of these carbon nanocolumn arrays evaluated in a three electrode system in nonaqueous electrolyte suggests that PLD technique is an ideal method to fabricate carbon nanocolumn array based microelectromechanical systems for 3D microbatteries.

2. Experimental

2.1. Preparation of carbon nanocolumn arrays by PLD technique

Carbon nanocolumn arrays were prepared on a titanium substrate following the procedures reported previously [19,20]. Typically, titanium foil was washed thoroughly with acetone in a sonication bath and then placed into a PLD chamber, close to the graphite target and at an off-axial position with respect to the target. A laser beam with a wavelength of 355 nm from a Q-switched Nd:YAG laser (Continuum, Precision 8000), operated at 10 Hz with 80 mJ pulse^{-1} and a pulse width of 7 ns was applied and focused on the target surface with a diameter of 1.5 mm. The substrate and target were rotated at 30 and 30 rpm, respectively. PLD was carried out at a base pressure of 2.66×10^{-4} Pa and a background N_2 pressure of 6.7 Pa. The PLD process was carried out for 90 min for carbon deposition.

2.2. Characterization

The morphology of the carbon nanocolumn arrays was characterized by scanning electron microscopy (SEM) performed on a field-emission scanning microscope (FESEM; Hitachi S-4800) operating at 15 kV. Transmission electron microscopy (TEM) images were recorded using a JEOL 2010F microscope operated at 200 kV. The composite and chemical states of the sample were examined on an X-ray photoelectron spectroscope (XPS, PHI 5600ci).

2.3. Electrochemical measurements

A conventional three-electrode cell was assembled in an argon filled glove box to examine the electrochemical performance of the sample. Carbon nanocolumn arrays on titanium foil were used as the working electrode without further treatment, while Li metal pressed on a nickel mesh was used as the reference and counter electrodes. The electrolyte used is 1 M LiClO$_4$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC = 1/1, v/v). Galvanostatic discharge–charge measurements were performed at room temperature within voltage limits of 3.5–0.01 V (vs. Li$^+$/Li) under a constant current density of 0.1 A g^{-1}.

3. Results and discussion

The morphology of the carbon nanocolumn arrays deposited on a titanium foil by the PLD technique at room temperature is observed by FESEM (Fig. 1). Side-view SEM image shows that the nanocolumns align perpendicularly to the surface of the titanium foil, suggesting that nanocolumns grow vertically on the substrate (Fig. 1a). The diameter of these nanocolumns is ranging from 50 to 100 nm, while the length is approximately 2.0 μm, giving a high aspect ratio of over 20:1. The aspect ratio of the nanocolumns is higher than that of the carbon microcolumns prepared by the pyrolysis of a patterned photoresist [17]. Given the fact that the nanocolumns grow with deposition time, the aspect ratio of the carbon nanocolumns can be well controlled. Thus, the PLD technique is superior over the pyrolysis of a photoresist in the fabrication of

carbon materials with controllable aspect ratio. Top-view SEM image shows rough surface of the sample due to the small cracks formed among the nanocolumns (Fig. 1b).

TEM images of the carbon nanocolumns scratched off the titanium foil are presented in Fig. 2. Low magnification TEM image shows that the nanocolumns are composed of small carbon grains, indicating that these nanocolumns possess a porous structure with high surface area. The selected area electron diffraction (SAED) pattern inset in Fig. 2a suggests the amorphous nature of these carbon nanocolumns. HRTEM image shown in Fig. 2b reveals that the nanocolumns are composed of curved carbon sheets lying parallel to the substrate. This result might suggest that the nanocolumns grows layer-by-layer during the PLD process. When carbon target is irradiated by a laser beam with an energy level exceeding its threshold in vacuum, carbon and electrons are released into the chamber. After the collision with N_2, the background gas, carbon deposits uniformly onto the surface of the substrate layer-by-layer. During this process, some of the carbon released from the target reacts with the residual oxygen species, leading to the formation of —C—O— bonds which have been detected by the XPS technique. The spacing among the graphite sheets is approximately 0.65 nm, larger than that of graphite. The large spacing and the absence of obvious graphite domains with well-aligned graphene layers indicate the amorphous nature of these carbon nanocolumns.

The XPS technique is an effective method in the determination of the identity of the elements and impurity present on the surface of a material [21]. XPS spectra of the carbon nanocolumn arrays are shown in Fig. 3. In addition to carbon, oxygen is also detected in the spectrum. These oxygen atoms are introduced by the surface absorbed O_2. The reaction of carbon with O_2 leads to the formation of various —C—O— bonds. These bonds provide plenty of active sites for the reaction with Li. The intensity of the binding energy is linearly proportional to the content of sp^3 and sp^2 bonds [21], which can reflect the nature of carbon materials. The XPS C 1s spectrum of the sample is well fitted with three Gaussian–Lorentzian curves (Fig. 3b). The curves centered at 283.9, 284.8, and 286.4 eV are ascribed to sp^2-bonded C, sp^3-bonded C, and —O—C— bonds, respectively. The area ratio of two peaks at 283.9 and 284.8 eV which reflects the sp^2/sp^3 ratio in the film is approximately 5.9, indicating that most of C in these carbon nanocolumns are sp^2-bonded and these nanocolumns have plenty of graphite sheets, as observed in the HRTEM image.

Carbon electrode with high aspect ratio is essential for the fabrication of 3D microbatteries with satisfactorily high specific capacity. Carbon nanocolumns with high aspect ratio of over 20:1 are promising candidates as electrode for 3D microbatteries. The electrochemical performance of these carbon nanocolumns is evaluated through galvanostatic discharge/charge experiments. Fig. 4a shows the discharge–charge profiles of the nanocolumns at a current density of 0.1 A g^{-1}. A long distinct plateau at the voltage range of 0.7–1.0 V is observed in the first discharge profile, which is associated with the formation of a solid electrolyte interphase (SEI) [22]. In contrast to that of well-graphitized carbon materials, no obvious plateaus are observed in the lower voltage range of 0.0–0.2 V in the discharge profiles of the carbon nanocolumns. The absence of the plateaus at the low voltage range is characteristic for disordered or nanosized carbon materials [9,12,23]. The first discharge capacity of the nanocolumns is approximately 1060 mAh g^{-1}, much higher than the theoretical value of graphite, 375 mAh g^{-1}. Generally, carbon materials with disordered structures can store more lithium ions due to their higher specific surface area [24]. It is reasonable that the specific capacity of the nanocolumns exceeds the theoretical value of graphite. Large irreversible capacity and low coulombic efficiency due to the electrolyte decomposition and the formation of a SEI on the electrode surface are typical for the disordered carbon materials. However, the reversible
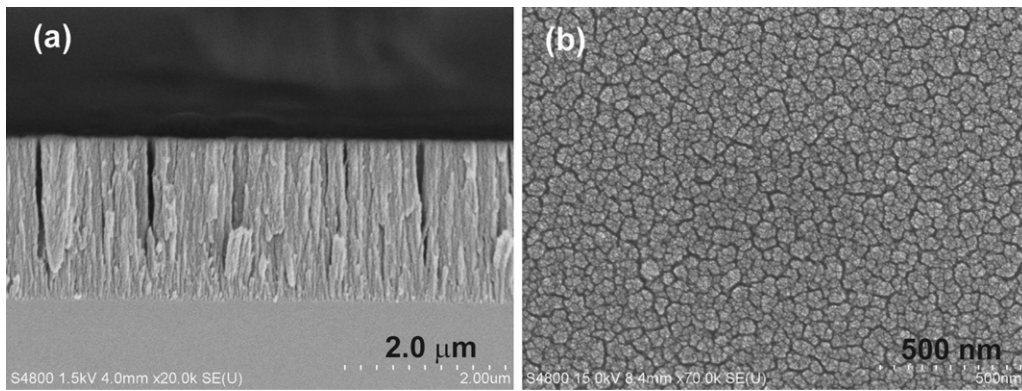
Fig. 1. FE-SEM images of the carbon nanocolumn arrays prepared using a PLD process. (a) Side and (b) top view.
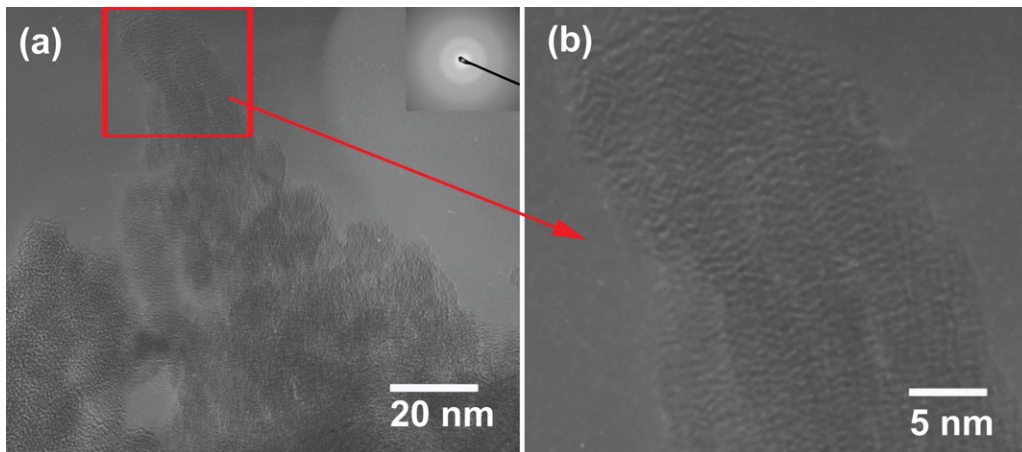

Fig. 2. (a) Low and (b) high-magnification HRTEM images of the carbon nanocolumns. The inset in (a) is the corresponding electron diffraction pattern.

capacity of these nanocolumns is as high as 670 mAh g^{-1}, giving a coulombic efficiency of about 63%. The high initial coulombic efficiency makes these carbon nanocolumns superior over other C-MEMSs, such as carbon posts [17] and carbon micro-net films [18] fabricated by the pyrolysis of a negative photoresist. The coulombic efficiency increases dramatically with discharge–charge cycles (Fig. 4b). Over 96% and 99% can be achieved in the second and fifth discharge–charge cycles, respectively.

The cycleability of the carbon nanocolumns upon Li insertion/extraction is an important factor that has to be evaluated when considering the potential application of these materials in 3D microbatteries. Fig. 5 shows the profiles of the discharge and charge capacities of the nanocolumns varying with the discharge–charge

cycles. These nanocolumns exhibit relatively good cycling stability. The reversible capacity decreases obviously over the first few cycles. After discharged and charged at a current density of 0.1 A g^{-1} for about 50 cycles, a reversible capacity of approximately 315 mAh g^{-1} is retained, approximately 52% of initial charge capacity. The reversible capacity after 50 cycles is still comparable with that of graphite, which can meet the demands of many microelectronic devices.

The high reversible capacities and good cycleability are attributed to the unique structure of the carbon nanocolumns (Scheme 1). These nanocolumns with high aspect ratio ensure high electron conductivity, fast lithium ion diffusion, and large lithium ion storage capability. During the PLD process, the carbon
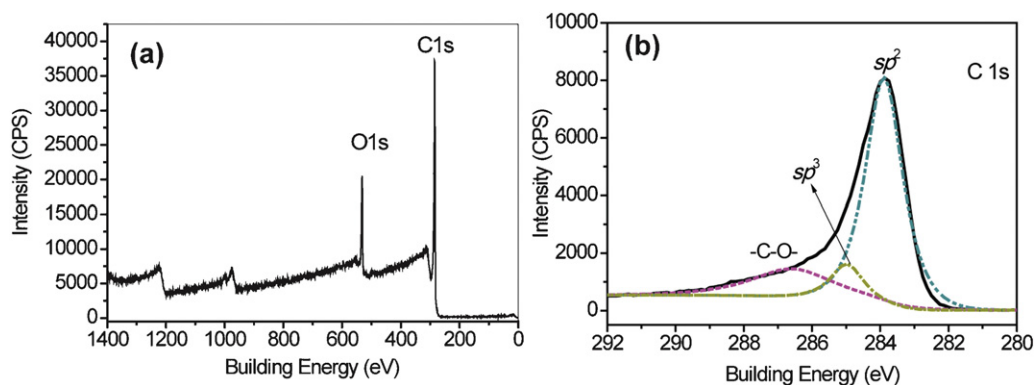

Fig. 3. XPS spectra of the carbon nanocolumn arrays. (a) The survey spectrum, and (b) C 1s peak with fitting curves.
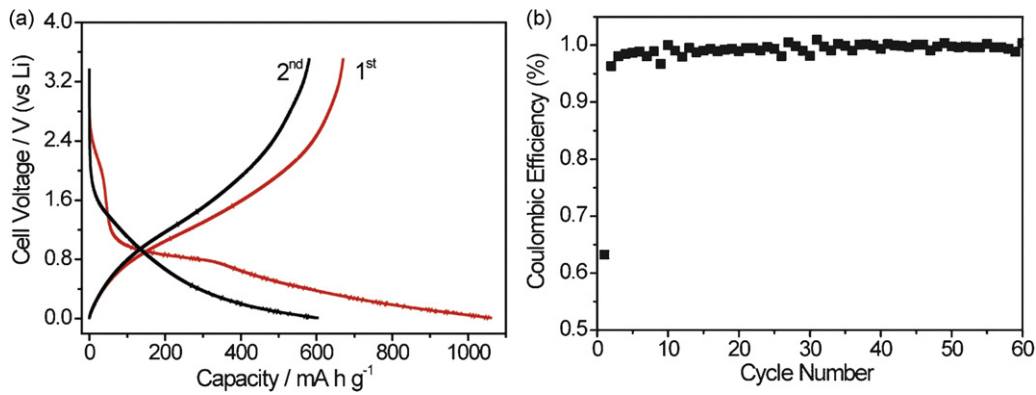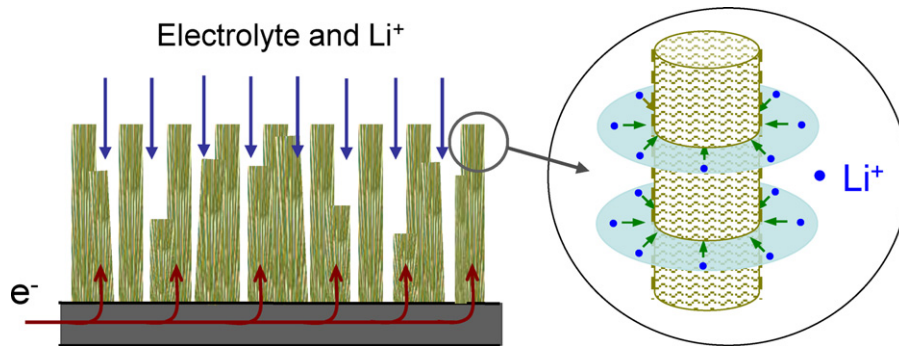
Fig. 4. (a) The first and second galvanostatic discharge–charge profiles, and (b) the coulombic efficiency of the carbon nanocolumn arrays at a current density of 0.1 A g^{-1}.

Scheme 1. Schematic representations of the transport of the lithium ions, the electrolyte molecules and electrons within the carbon nanocolumn array electrode, and the insertion of lithium ions into a nanocolumn.

nanocolumns are deposited onto the surface of titanium foil layer-by-layer directly, guaranteeing good contact to the substrate. The good contact of the nanocolumns to the substrate, and the graphite sheets in the nanocolumns ensure fast electron conductivity within the electrode. As observed in the top view SEM image, plenty of cracks form during the PLD deposition process. These cracks provide pathways for the penetration of the electrolyte and lithium ions, and at the same time accommodate the volume variation of the electrode during the lithium insertion/extraction. The diameter of these columns is within several tens nanometer, shortening the diffusion distance of lithium ions. It is also noted that the curved

graphite sheets are stacked perpendicular to the longitudinal axes of the columns. This type of stacking and the large spacing of the graphite sheets greatly facilitate the insertion of the lithium ions from the side of the columns. However, as revealed by the XPS spectra, some —C—O— bonds exist in the carbon nanocolumns. These —C—O— bonds are supposed to facilitate the formation of SEI film on the surface of the carbon nanocolumns at a voltage range of 0.7–1.0 V, resulting in the relatively high irreversible capacity and the fast capacity decay over the first few cycles.

4. Conclusion

Carbon nanocolumn arrays with aspect ratio as high as 20:1 have been deposited directly on a titanium foil by a PLD technique at room temperature. Given the fact that plenty of curved graphite sheets stacked parallel to the substrate in the columns, it can be concluded that the carbon columns are growing in a layer-by-layer manner during the PLD process. The first discharge and charge capacities of these carbon columns at a rate of 0.1 A g^{-1} are approximately 1060, and 670 mAh g^{-1}, respectively, giving a coulombic efficiency as high as 63%. After discharged and charged for about 50 cycles, a reversible capacity of approximately 315 mAh g^{-1} is still retained. The large reversible capacity, high coulombic efficiency and good cycleability are attributed to the unique structure of these carbon columns. The parallel stacked graphite sheets in the columns, the small diameter of the columns, the void space among the columns, and the well contact of the columns to the substrate ensure fast electron, lithium ion, and electrolyte transportation. The good electrochemical performance of the carbon columns
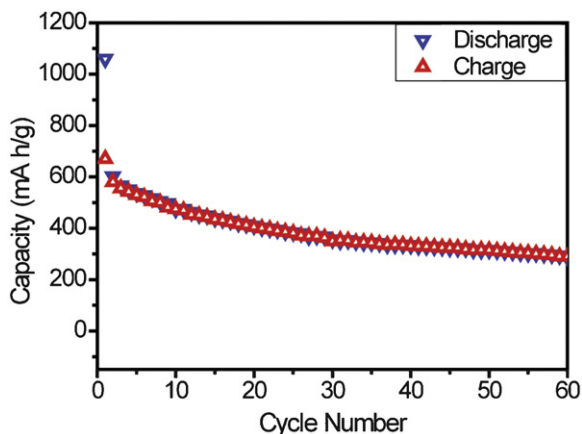

Fig. 5. The cycling performance of the carbon nanocolumn arrays.

suggests that the PLD technique is a promising approach to construct 3D carbon microelectrode with high aspect ratio for microbattery applications.

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