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Free standing electrospun carbon nanofibers-A high performance anode material for lithium-ion batteries

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Abstract

Free standing carbon nanofibers (CNFs) are prepared by the carbonization of polyacrylonitrile using a simple electro-spinning technique. The electro-spun fibers are studied as an anode material for lithium-ion batteries in half-cell configurations. The fibers showed an initial discharge capacity of 826 mAh g⁻¹ at a current density of 200 mA g⁻¹ and exhibited an appreciable capacity profile during cycling. The Li-storage mechanism has been explained based on cyclic voltametric and galvanostatic cycling results.

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Introduction

Carbon based materials, especially graphite, are dominant in the battery industry as an anode material for lithium-ion power packs. Looking specifically at graphite, this is due to its overwhelming advantages such as ease availability, good reversibility with high Coulombic efficiency and an appreciable capacity (372 mAh g^{-1})[1-3]. Furthermore, the lower insertion potential of Li^+ provides a high energy density of the cell ($\sim 150 \text{ Wh kg}^{-1}$ and $\sim 400 \text{ Wh dm}^{-3}$). However, state-of-the-art lithium-ion batteries suffer from the processing cost, durability and safety issues relating to electric vehicle (EV) and hybrid electric vehicle (HEV) applications[4]. The operating potential of a graphitic anode is very close to metallic lithium, in which dendrite formation could be unavoidable, particularly at high current rates. Thus, other carbon nano-structures such as carbon nanotubes[5, 6], nanofibers[7], graphene[8, 9], activated carbons[10] and composite with other transition metal elements[11] have been proposed as alternatives to their high power applications, stated above[12]. Apart from nanofibers, the counterparts suffer in various aspects, like higher insertion potential in composites, high cost, poor cycle-ability, the difficulty to achieve theoretical capacity etc.,[13, 14]. The carbon nanofibers (CNFs) can accommodate more lithium than conventional intercalation mechanism (LiC_6) in graphite due to their turbo-static storage behaviour [15]. So far, only a few reports are available on the lithium storage behaviour of CNFs prepared by various synthetic routes, such as pyrolysis [15], electro-spinning [7], vapour growth [16] etc. To the best of our knowledge, no extensive studies has been carried out on the electro-chemical performance CNFs for prolonged cycling relatively at high current rates, prepared by electro-spinning. This motivated us to synthesis the CNFs by electro-spinning technique. This technique has been extensively explored for the fabrication of long and continuous nanofibers because of its ease and low cost. It has also been

demonstrated that a variety of materials, such as polymers, metal oxides with various morphologies and carbons could be made into nanofibers by this efficient, simple and inexpensive technique [17, 18].

Experimental

Polyacrylonitrile, PAN ($M_w = 150,000$) and dimethyl formamide (DMF) were purchased from Aldrich and used as received without any further purification. In the typical synthesis, 1 g of PAN was dissolved in 10 ml of DMF and the solution was stirred for 24 h at room temperature to form a homogeneous pale white colour solution. Later, this prepared solution was introduced into a 10 ml syringe with a hypodermic needle (diameter 27 G) in a controlled electro-spinning setup (ELECTROSPUNRA, Singapore). The flow rate and applied electric field was varied to obtain the optimal conditions to yield nanofibers, for example a flow rate of 1.2 ml h^{-1} and an applied electric field of 1.5 kV cm^{-1} . The distance between needle tip and collector against the applied electric field was set as 14 cm, which aided the stretching of the jet due to an increase in the distance covered by the spiralling electro-spun jet before being deposited on the collector. The fiber mesh obtained shown in Fig. 2(a) was then stabilized in the air for 250°C for 30 min to facilitate the removal of other organic moieties. The heating and cooling rate of the stabilization process were maintained as 1 and 3°C min^{-1} , respectively. As the electro-spun fiber mainly consisted of hydrocarbon, the removal of the hydrogen atoms predominately leaves carbon in the stabilized nanofibers. These stabilized nanofibers were later carbonized at 800°C for 1 h in the N_2 inert atmosphere to obtain CNFs (figure 2(b)). The heating and cooling rates of the carbonization process were maintained as 3 and 5°C min^{-1} , respectively. The obtained carbon fibers were later employed for electrochemical studies.

Powder x-ray diffraction was used to study the structural properties of prepared CNFs by Bruker AXS, D8 Advance with $\text{Cu K}\alpha$ radiation. Morphological features and the internal

structure of the synthesized powders were recorded using a scanning electron microscope (FESEM, JEOL JSM) and a transmission electron microscope (TEM, JEM-2010, JEOL USA Inc.), respectively. A Raman spectrum was recorded using a micro-Raman spectrometer (Horiba-JY T64000) in a backscattering configuration with an excitation wavelength of 532 nm and a power of 1 mW. The backscattered signal was collected through a 50 $\times$ objective with a laser beam measuring 2 μ m. All the electrochemical studies were conducted in a two-electrode standard coin cell (CR 2016) configuration in ambient temperature conditions. The composite anode were formulated with an exactly weighed 10 mg of active material (CNF), 1 mg of super P, and 2 mg of binder (Teflonized acetylene black, TAB-2). Then, it was pressed on a 200 mm² copper mesh (thickness 0.25 mm, Goodfellow, UK), which served as a current collector. It was dried at 60 °C overnight before conducting cell assembly under an Ar filled glove box. The electrodes were separated by a microporous glass fiber separator (Whatman, Cat. No. 1825-047, UK) and 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 wt.%, DAN VEC) was used as the electrolyte solution. Cyclic voltammetric (CV) traces were recorded using a Solartron, 1470E and a SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat in the two-electrode configuration, in which metallic lithium was used for both the counter and reference electrodes. Galvanostatic cycling performances were recorded in the constant current mode between 0.005-3 V at a constant current of 200 mA g⁻¹ using an Arbin 2000 battery tester.

Results and discussion

The powder x-ray diffraction pattern of CNF is shown in figure 1(a). Two broad peaks around $\sim 25^\circ$ (0 0 2) and $\sim 42^\circ$ (1 0 0) are signatures of carbon with a typical nanocrystalline structure. Dahn *et al.*[15], proposed an empirical parameter (R) to estimate the number of carbon nanosheets arranged in a single layer. The parameter R corresponds to the ratio of height of (0 0 2) reflection to the background, which is illustrated in figure 1(a). The

parameter R is calculated as 2.17 and this indicates a relatively higher degree of graphitization, which suggests a larger concentration of the parallel single layers in carbon materials. Besides, it is well known that carbon with higher graphitization and a better crystallite structure enables better electronic conductivity profiles. Figure 1(b) represents Raman spectra for electrospun CNFs recorded from 800 to 2000 cm^{-1} for the analysis of the nature of carbon formed during carbonization. The Raman spectrum clearly shows the characteristic vibrational modes at ~ 1355 and ~ 1590 cm^{-1} corresponding to D and G bands of carbon, respectively[19]. More clearly, D peak at ~ 1355 cm^{-1} corresponds to a breathing mode or k -point photons of A_{1g} symmetry, and a relatively weak G line at ~ 1590 cm^{-1} , which should be assigned to the in-plane bond-stretching motion of pairs of C sp^2 atoms (the first order scattering of the E_{2g} photons). It is worth mentioning that both the G and D bands are not clearly distinguished like graphite (which exhibits a sharp line ~ 1590 cm^{-1}). This result suggests CNFs comprising partially graphitized carbon along with amorphous carbon in the prepared CNFs. The graphitized carbon generally consists of assemblies of graphitic layers, which are expected to act as a good host for the storage of lithium ions. The peak intensity ratio of D/G bands plays a crucial role in determining the degree of the crystalline nature of carbon structures, which is important for electrochemical lithium storage. According to the literature [20-22], the lower the intensity ratio of D/G bands, the higher the electronic conductivity, and the ratio is calculated 1.22 in the present case. The observed values are consistent with the previous report on carbon micro-tubes by chemical vapour deposition by Meduri et al.[23].

Surface morphological features and the internal structure of electrospun CNFs are given in figure 2. Figures 2(a) and (b) represent optical images of the fibres before and after sintering in a N_2 atmosphere at 800 $^{\circ}\text{C}$, respectively. It is obvious that the spun fibre retains its fibrous morphology after the sintering process though it has shrunk in size. In order to

ensure the retention of such fibres, an SEM has been recorded for both fibres and the results are presented in figures 3(c) and (d). The SEM images show the highly interconnected networks of as-spun and sintered fibers with variation in fibre's diameter. The variation in fiber diameter is quite acceptable, since during the sintering process accompanied with gas evolution (e.g. CO, CO₂, H₂O etc) it forms free standing CNFs. In order to study the internal structure of CNFs, TEM has been recorded and presented with a selected area electron diffraction (SAED) pattern in figures 2(e) and (f). The TEM image shows fibres with a diameter of ~200 nm without a porous structure. The SAED pattern shows the appearance of diffuse rings, which is indicative of the amorphous nature of the material prepared. This SAED results corroborates the XRD and Raman measurements.

Figure 3(a) represents the cyclic voltammogram of the Li/CNF cell between 0.005-3 V at a scan rate of 0.1 mV s⁻¹. The cell shows an open circuit potential of ~2.9 V and first discharged to a lower cut-off potential to insert the lithium; the cell was subsequently charged to extract the lithium from the CNFs. During the second cycle, a similar reaction took place, however a huge reduction in the area under the curve was observed when compared to the first cycle. CV traces of rest of the cycles are consistent with each other, except for the first cycle. It is well known that a solid electrolyte interphase (SEI) formation takes place ~0.7 V versus Li, particularly on carbonaceous anodes [3]. From figure 3(a), it is clear that the decomposition continues until 0.46 V versus lithium for SEI and it mainly comprises polycarbonate, polyethylene oxide and some inorganic products, which consume of excess lithium in the first cathodic sweep. This clearly indicates the reduction process of Li-ions and its reactivity towards defects available in CNFs [16]. Moreover, the reaction involves formation of SEI, which is irreversible; this is apparent when compared to subsequent cycles. As discussed earlier, the CNFs comprise partially graphitized carbons (formed by the assembly of graphitic layers) along with amorphous carbon. More clearly, a reduction

potential below ~ 0.5 V corresponds to the lithium binding on the basal plane of graphitic layers. In such process, lithium can be adsorbed on both sides of layers, which leads to two layers of lithium with the theoretical capacity of 744 mAh g^{-1} via the possible formation of Li_2C_6 [8]. In the anodic sweep, above ~ 0.5 V is ascribed to the faradic capacitance on the surface or on the edge-sites of graphitic sheets composed by CNFs.

Galvanostatic charge-discharge profiles of Li/CNF cells were recorded between 0.005-3 V at current density of 200 mA g^{-1} in room temperature and are given in figure 3(b). The Li/CNF cell delivered an initial discharge capacity of 826 mAh g^{-1} at 200 mA g^{-1} current density. However, during the subsequent charge 417 mAh g^{-1} , capacity only reversibly obtained. The irreversible capacity loss is almost half of the initial discharge capacity obtained. During the first discharge, the cell showed flat potential region of ~ 0.5 V and this may related to the adsorption of lithium ions on the surface of the fibers or nanosheets of graphitic layers so-called pseudocapacitive storage [1, 15, 16]. At the same time, the cavities between nanosheets, due to scrolling and crumpling, could also contribute to the excess lithium consumption [1, 16]. According to the micropore mechanism[15], the extraction of lithium from the cavities has to go via the graphitic domains. The reaction between lithium ions and the carbon nanostructures results in an appreciable voltage hysteresis during the charge process. The SEI formation and the defects in the fibres also consume lithium during the first discharge; this cannot be excluded, whereas a Li/CNF cell delivered a capacity of 370 and 350 mAh g^{-1} for the second discharge and charge, respectively. The obtained discharge capacity in second cycle is almost the same as the theoretical capacity of graphite (372 mAh g^{-1}) with the Coulombic efficiency of $\sim 95\%$. This clearly indicates the maximum amount of lithium that can be stored in CNFs according to the composition LiC_6 during cycling, except for first cycle. More importantly, easy reversible storage of lithium can be achieved in CNFs rather than intercalation mechanism in graphitic anodes, which is

necessary for high power density of the cell.

Cycling profiles of Li/CNF cells at current density of 200 mA g^{-1} are represented in figure 4(a) with Coulombic efficiency. It can be seen that, the discharge capacity is fading during cycling and this kind of fading is expected in partially graphitized fibers. At the end of the 200th cycle, the cell delivered the discharge capacity of 143 mAh g^{-1} , which is 39% of capacity retention calculated from the second cycle. It is noticeable from figure 4(a) that the Coulombic efficiency of the Li/CNF nanofiber cell is almost 100% except for the few initial cycles, which indicates excellent reversibility during galvanostatic cycling. In subsequent cycles, the adsorbed lithium reacts with CNFs and loses the available active surfaces, which leads to a capacity fade. However, similar reports are available on CNFs based materials, for example Kim *et al.*[7] reported the performance of CNFs obtained from PAN by electrospinning and carbonization at 700°C . The Li/CNF cells showed a reversible capacity of 300 mAh g^{-1} at the low current density of 30 mA g^{-1} in the first cycle: no cycleability was reported. Vapour-grown CNFs exhibited a reversible capacity of $\sim 450 \text{ mAh g}^{-1}$ with a huge irreversible loss ($\sim 900 \text{ mAh g}^{-1}$) at a current rate of 0.1 C by Subramanian *et al.*, [16]. Li *et al.*[13], also reported porous carbon fibers derived from the conducting polymers, which showed a reversible capacity of $\sim 330 \text{ mAh g}^{-1}$ at the 0.5 C rate. This clearly indicates the obtained results are comparable with previously published results. Further studies are in progress to suppress the irreversible capacity loss and improve the capacity profile without fading during a prolonged cycle. High power applications, such as EV and HEV, required a high rate performance while employing an anode. Hence, a Li/CNFs cell has been made to study the rate capability at different current densities, from 150-900 mA g^{-1} between 0.005-3 V in room temperature, and these are presented in figure 4(b). The test cell delivered discharge capacity of 442, 273, 198, 166, 142 and 125 mAh g^{-1} at current density of 150, 300, 450, 600, 750 and 900 mA g^{-1} , respectively. The obtained capacity values were expected

and the low current performance (150 mA g^{-1}) reflects the cycling performance obtained above. On the other hand, the test cell retained the discharge capacity (375 mAh g^{-1}) while switching back to 150 mA g^{-1} . In all the current densities, Coulombic efficiency is found to be over 99%. The charge-discharge curves and CV traces clearly indicates the adsorbing behaviour of Li-ions on the surface of CNFs. Such pseudocapacitive storage behavior certainly improves the high power capability of Li-ion power packs, which results in the possibility of using them in high power applications, such as with anodes EV and HEV. However, long-term cycleability is the main concern for CNFs, irrespective of the synthesis procedures employed. Further studies are in progress to improve the cycleability of the CNFs using a simple and scalable electro-spinning method.

Conclusion

To conclude, a simple electro-spinning technique has been adopted to synthesis CNFs derived from PAN. X-ray diffraction and Raman studies revealed that the CNFs comprise partially graphitized carbons. SEM and TEM pictures showed the fibrous nature of carbon before and after sintering. The electrochemical lithium storage properties were evaluated by means of a half-cell configuration with lithium and showed discharge capacity of 826 and 370 mAh g^{-1} for the first and second cycle respectively, at a current density 200 mA g^{-1} . Capacity fading is encountered during prolonged cycling of 200 cycles.

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Figure captions

- Figure 1 (a) Powder x-ray diffraction pattern of electrospun CNFs sintered at 800 °C for 1 h under Ar flow, and (b) Raman spectrum of CNFs.
- Figure 2 (a) (b) Optical images of as-spun and fibers sintered at 800 °C for 1 h under Ar flow (CNFs), respectively; (c), (d) scanning electron microscopic images of as-spun and CNFs, respectively; (e) high-resolution transmission electron microscopic images of CNFs; (f) SAED pattern of CNFs.
- Figure 3 (a) Cyclic voltammogram of Li/CNF cells cycled between 0.005 -3 V at scan rate of 0.1 mV s⁻¹, in which lithium act as both counter and reference electrodes, and (b) typical galvanostatic charge-discharge curves of a Li/CNF cell recorded at current density of 200 mA g⁻¹ in ambient temperature conditions.
- Figure 4 (a) Galvanostatic cycling profiles of Li/CNF recorded with at current density of 200 mA g⁻¹; (b) rate capability studies of a Li/CNF cell with different current densities from 150 to 900 mA g⁻¹.

Figure 1

Figure 2

Figure 3

Figure 4