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Cellulose Nanofibers as Carbon Source for Rechargeable Batteries

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Abstract

Carbon nanofibers have been studied as a promising electrode candidate for energy storage devices. However, expensive petroleum-based polyacrylonitrile (PAN) has been extensively used as carbon source in carbon fiber production. Here, cellulose acetate nanofibers were presented as low cost, environmentally friendly carbon source. Carbon nanofibers (CNFs) were produced by electrospinning of cellulose acetate followed by carbonization. In addition, TiO_2 nanoparticles were incorporated in order to improve electrochemical performance of Li-ion and Na-ion cells. Electrospraying/electrospinning approach was utilized to fabricate nanocomposite electrodes. The cell containing TiO_2/CNFs delivered the high specific capacities of 260 mAh/g and 150 mAh/g with high Coulombic efficiencies, respectively, in Li-ion and Na-ion batteries. These results prove that cellulose could be used as a cheap and green carbon source in rechargeable batteries and electrospraying/ electrospinning technique is a promising approach to develop nanostructured electrode materials with high capacity and good cycling performance.

Keywords: *carbon; cellulose; nanofibers.*

1. Introduction

There is great demand for Li-ion batteries in many applications including portable electronic devices, electric vehicles and smart grids because of long cycle life and high energy density. However, high cost and limited lithium resources are restricting the usage of lithium batteries. Therefore, high-performance earth abundant metal ion batteries including Na-ion batteries have received increasing attention. Due to the features of low cost, non-toxicity, abundance and uniform distribution around the world, sodium ion batteries have been attracted great interest as alternative rechargeable batteries. Carbon materials have been studied in Na ion batteries and nanostructured materials have improved power and energy densities due to enhanced kinetics and large surface area [1-3].

Carbon nanofibers have attracted great attention because of their good mechanical strength, high electrical and thermal conductivities, and corrosion resistance for potential applications such as heat-management materials, composite reinforcement, high-temperature catalysis, membrane-based separation, and components for nano electronics and photonics. Nano-scale carbonaceous structures have also been commonly used in energy storage applications to increase cycle life and capacity [4, 5]. For example, nano structured carbon materials have been widely studied for supercapacitors. Pore structure of electrospun carbon nanofibers could be altered and it is possible to load active materials on these nanofibers, resulting high capacitance with long life span in energy storage systems [6].

Electrospinning has been a common method to prepare carbon nanofibers. In a typical electrospinning set up, polymer solution is charged by DC voltage due to potential difference between the syringe and grounded collector. When surface charge repulsion overcomes the surface

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tension, a jet is drawn through collector while it decreases the diameter and solvent evaporates. Finally, nano-sized fibers form nonwoven mat on the collector. In general, fiber diameter decreases with decreasing polymer concentration and increasing solution conductivity [6].

Polyacrylonitrile has been used as a precursor in fibrous carbon materials owing to good mechanical properties, spinnability and high carbon yield. PAN fibers were generally stabilized at 280 °C in air and carbonized at a temperature of 600–1100 °C in inert atmosphere. However, PAN is a petroleum-based polymer and it is very expensive. Therefore, there is a tremendous interest worldwide in developing carbon materials from renewable biomass. Cellulose is an abundant substance in nature and could be used as a low cost environmentally friendly carbon source [6-9]. Until now, limited efforts have been reported on natural carbon sources. Park et al [10] investigated nanocellulose reinforced PAN and they confirmed that cellulose could reduce the energy consumption by lowering carbonization temperature. Lai et al [11] reported lignin as a carbon source and the resultant carbon nanofibers were used in supercapacitors. The high capacitance of 64 F g^{-1} was reached at the current density of 400 mA g^{-1}. Zhou et al [12] presented spider silk as carbon nanofiber precursor as sustainable electrocatalysts for microbial energy harvesting. Hao et al [1] presented chitin as a carbon source and use them in potassium ion batteries which led to promising results.

Herein, we presented carbon nanofibers via electrospinning of cellulose acetate and subsequent carbonization. TiO_2/CNFs were prepared by electrospraying and the resultant composite was used in Li-ion and Na-ion cells.

2. Experimental set up

Figure 1 shows the schematic of sample preparation. First, cellulose acetate was dissolved in dimethylacetamide/tetrahydrofuran (DMAc/THF) with the volume ratio of 2 to 1 to obtain cellulose acetate solution. 10 wt% CA was dissolved in a solvent mixture overnight and the resultant solution was used for electrospinning. During electrospinning, the voltage of 20 kV was applied and the distance between the collector and the syringe was 16 cm. Electrospinning and electrospraying techniques were used to prepare TiO_2/CA nanofibers and the voltage was applied on both polymer solution and nanoparticle dispersion during the process. The resultant nanofiber mats were dried at 60 ºC to remove the remaining solvent from nanofibers. After that, heat treatment was applied to obtain CNFs and hybrid TiO_2/CNFs. CA and CA/TiO_2 nanofibers were carbonized at 800 ºC for 2 hours to obtain carbon nanofibers. The obtained CNFs were used as electrodes in Li and Na ion cells.

3. Results and Discussion

Figure 2 shows SEM images of CNFs and TiO_2/CNFs. Bead free nanofibers were obtained for CNFs and electrospraying/electrospinning technique provided uniformly distributed TiO_2 nanoparticles on CNFs. Smooth nano-sized carbon nanofibers derived from cellulose was also reported by Gaminian et al [13] for supercapacitors.

Nanostructure of electrodes determines the electrochemical properties of batteries. SEM images of TiO_2/CNFs show that nanoparticles uniformly distributed on fiber surfaces, which leads to enhanced electrochemical performance. Short ions diffusion path, reduced strain and enlarged electrode/electrolyte contact area could largely improve the electrochemical activity, resulting higher capacity with good cycling performance.

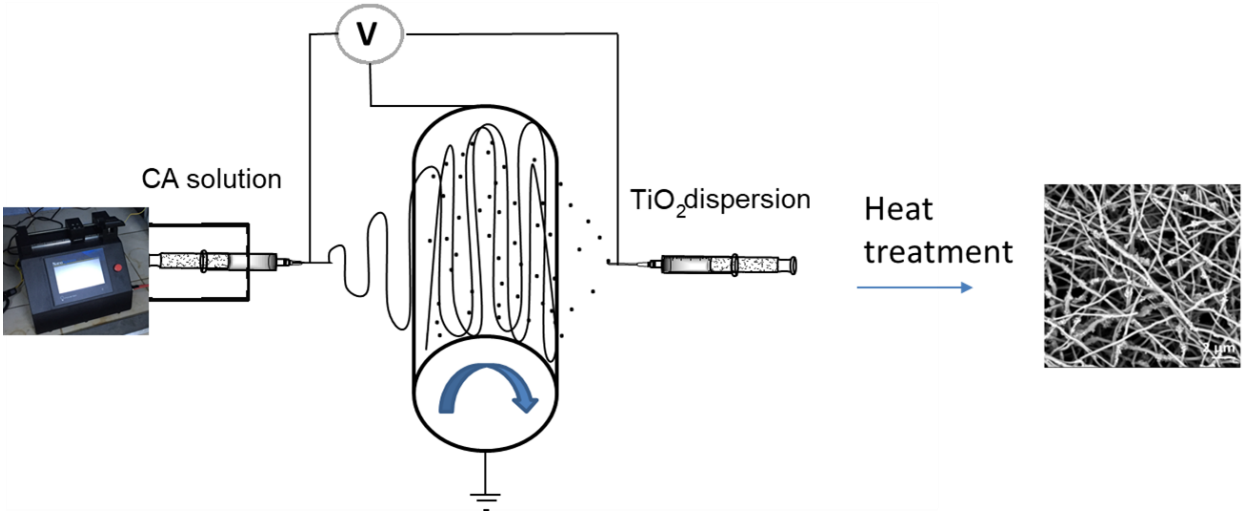

Figure 1. Sample preparation.

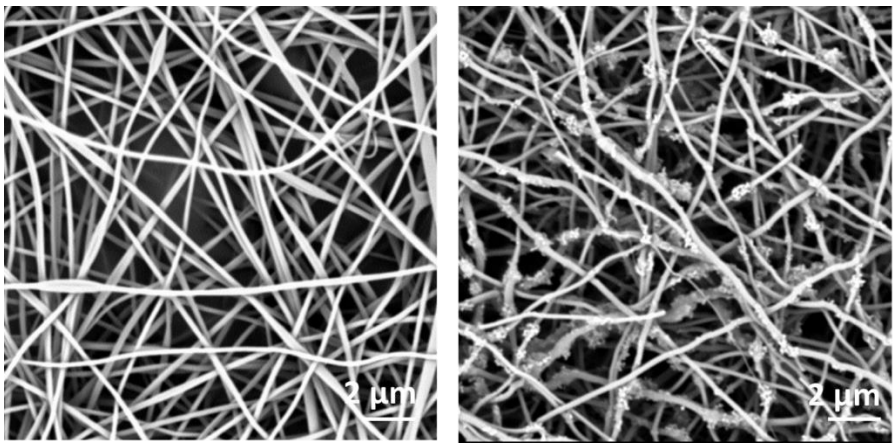

Figure 2. SEM images of CNFs and hybrid TiO_2/SNFs

In order to improve performance and reduce cost of the electrochemically active materials, it is vital to investigate inexpensive, and highly conductive nanostructured materials with high surface area. Using nanostructured electrodes have been reported to improve the Li-ion transport in electrode by shortening the Li-ion insertion/extraction pathway [14].

TiO_2 materials have attracted great attention owing to the characteristics of low cost, abundance and environmentally friendly nature and has been used in many applications including photocatalysis, solar cells, hydrogen storage and anode materials [15]. The theoretical capacity was calculated to be 268 mAh g^{-1} in lithium cells. Nanostructured TiO_2 materials could be synthesized by numerous methods; such as the template-assisted method, the sol–gel process, electrochemical anodic oxidation, and hydrothermal treatment [15].

Figure 3 displays specific capacity versus cycle number for the cell containing TiO_2/CNFs in Li-ion battery. We have synthesized TiO_2/CNF electrodes by using electrospraying/electrospinning techniques. The high specific capacitance of 260 mAh/g was seen during cycling test. Nanostructured electrodes enhance the kinetics so high capacity with good cycling performance was achieved. At the end of 100 cycles, high reversible capacity of around 260 mAh/g was seen

owing to nanostructured morphology. Crystal structure surface area and particle structure are effective on the reversible capacity and it can be concluded that electrospraying could be an effective method to prepare high performance electrode materials. Coulombic efficiency was also presented in Figure 2. The initial Coulombic efficiency was about 50% due to the decomposition of the electrolyte to form SEI. After the first cycles, Coulombic efficiency was over 98%, which indicating formation of thin SEI films on the surface and the stabilization of as formed SEI films during cycling.

Wang et al [14] reported TiO_2–graphene hybrid nanostructures and the specific capacity was found about 180 mAh/g. Li et al [16] studied graphene and TiO_2 hybrid via sol gel technique and the capacity of about 180 mAh/g was reported at 0.1A/g. Myung et al [15] reported the capacity of 225 $mAhg^{-1}$ at the 50th cycle.

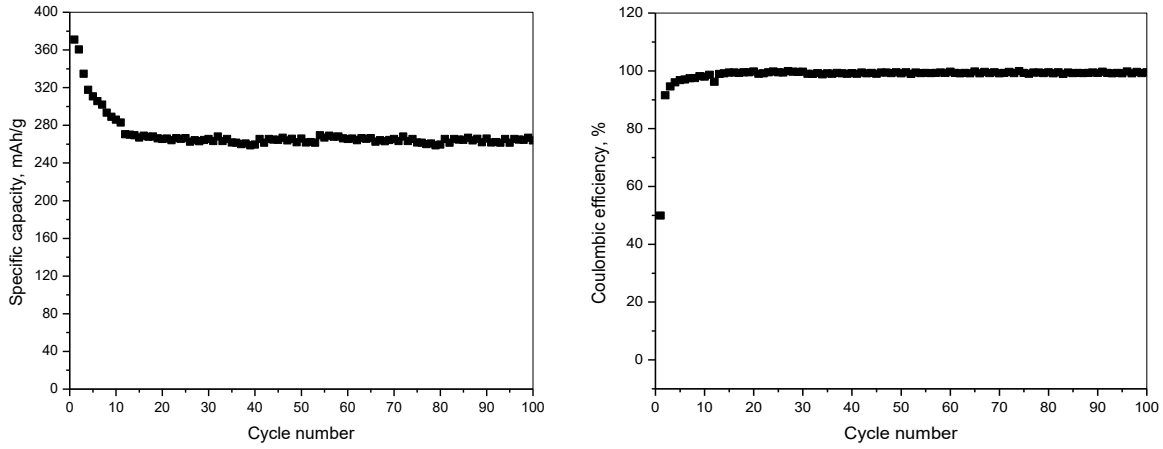

Figure 3. Cycling performance and Coulombic efficiency of hybrid TiO_2/CNFs in Li-ion battery.

Figure 4 displays specific capacity versus cycle number for the cell containing TiO_2/CNFs in Na-ion battery. The specific capacitance was observed above 150 mAh/g with excellent cycle life and high Coulombic efficiency indicating reversible Na ion uptake and release during cycling. Smaller particle size and nanostructured morphologies shorten the sodium ion diffusion distance and thus improve the capacity. The initial Coulombic efficiency was about 50% due to the decomposition of the electrolyte to form SEI. After the first cycles, Coulombic efficiency was over 98%, which indicates formation of thin SEI films on the surface and the stabilization of SEI films. At the end of 100 cycles, the capacity was observed at around 150 mAh/g. Xiong et al [2] reported amorphous TiO_2 nanotube anode and the specific capacity was also reported about 150 mAh/g in 15 cycles.

The typical discharge-charge curves were presented in Figure 5 for Li cell with TiO_2/CNFs. During discharging, the plateau around 1.8 V and the plateau at 1.9 V during charging was observed, which was related to the phase transition between the tetragonal and orthorhombic phases with Li insertion into TiO_2. Distinct potential plateaus appear at approximately 1.75 and 1.9 V in the discharge and charge curves, which corresponding to Li + insertion and extraction from the anatase structure. Similar result was also reported by Myung et al [15]. The discharge curve of TiO_2 can be separated into three parts; monotonic voltage decrease induced by a solid–solution insertion into the anatase phase (3–1.8 V), Li + insertion into the interstitial octahedral site of TiO_2 , where a two-phase reaction occurs with phase equilibrium of the Li-poor $Li_{0.01}TiO_2$

(tetragonal) phase and the Li-rich Li_2 TiO_2 phase (1.8–1.7 V), and slow decay of the voltage associated with capacitive lithium storage on the surface of the nanorods, as well as formation of Li_1TiO_2 phase (1.7–1 V).

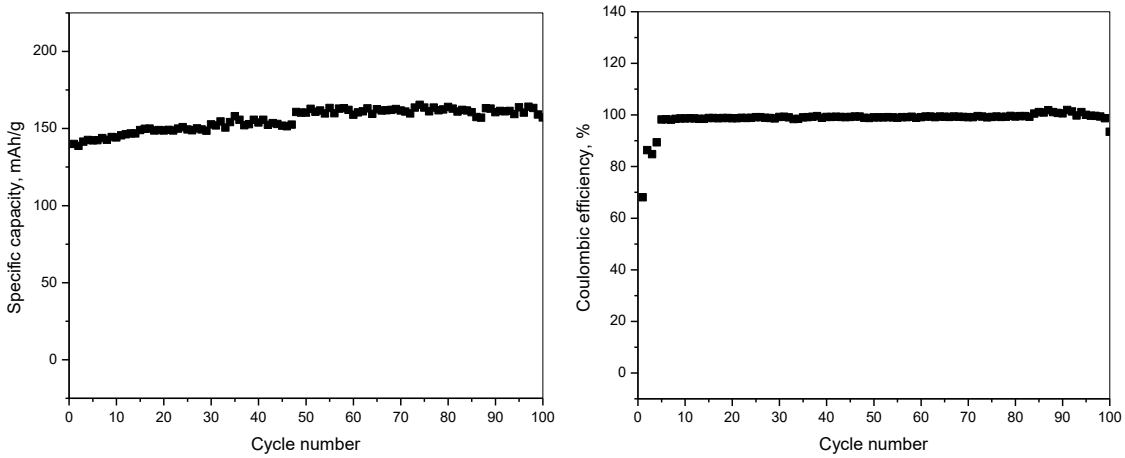

Figure 4. Cycling performance and Coulombic efficiency of hybrid TiO_2/CNFs in Na-ion battery.

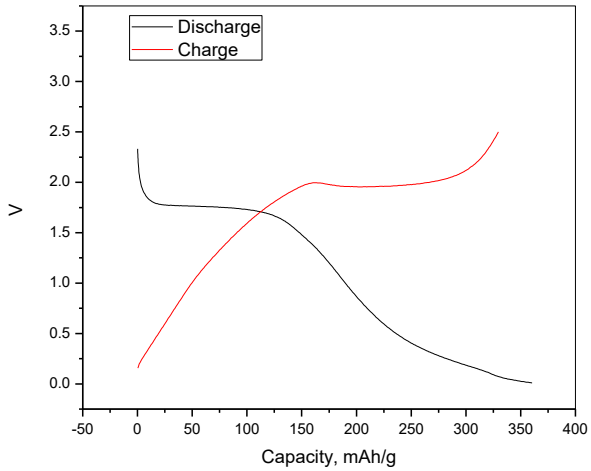

Figure 5. Discharge-charge curves of hybrid TiO_2/CNFs in Li-ion battery.

Typical discharge charge curves was presented in Figure 6. TiO_2 is a more convenient anode material for sodium-based energy storage systems over the lithium-based counterparts. In TiO_2, major lithium storage capacity is contributed by the voltage plateau at 1.75−2.1 V (vs Li/Li^+) in lithium cells, however the main capacity contribution for sodium ion is below 1 V (vs Na/Na+).

Similar curves was also reported by Wu et al [3] for TiO_2 nanoparticles electrodes. Even the theoretical capacity is 335 mAh g^{-1} for TiO_2 in Na ion batteries, slow sodium ion diffusion and low intrinsic electronic conductivity restrict their energy storage performance. However, electrochemical performance could be improved by designing nano-structured active material where sodium ion diffusion distance is shortened. He et al [17] also designed TiO_2/C nanostructured electrode and a high capacity of around 150 mAh/g was reported.

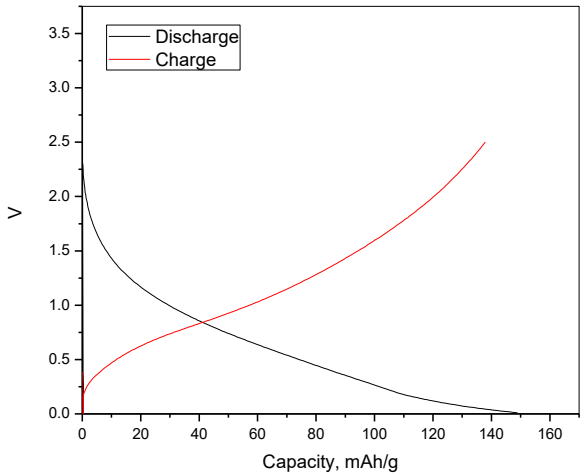

Figure 6. Discharge-charge curves of hybrid TiO_2/CNFs in Na-ion battery.

4. Conclusions

Facile, cheap and environmentally friendly approach was presented to fabricate carbon nanofibers. Carbon nanofibers were fabricated by pyrolyzing electrospun cellulose acetate nanofibers. The carbonization was occurred at 800 ºC for 2 hours. TiO_2/CNFs were obtained by combining electrospinning/electrospraying and carbonization techniques. The obtained composite had high capacity with good cycling performance in Li-ion and Na-ion batteries. It is, therefore, demonstrated that cellulose could be used instead of petroleum based PAN and electrospraying/electrospinning is a facile approach to fabricate high performance nanocomposite electrodes for rechargeable batteries.

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