



Research article

Carbon clusters decorated hard carbon nanofibers as high-rate anode material for lithium-ion batteries

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ABSTRACT

Hard-soft composite carbons have shown great potential as one of the most promising anode materials for fast rechargeable lithium-ion batteries (LIBs). However, there is still a lack of systematic research about the influence of hard and soft carbons on rate performance. In this work, the influence of carbon microstructure on Li⁺ and electron transfer has been investigated thoroughly by controllable introduction of coal tar pitch (CTP) to polyacrylonitrile (PAN) in the electrospun carbon nanofibers (CNFs). The result indicates that the CTP derived carbon clusters introduced into low crystallinity carbon influence the electron transport and solid-state Li⁺ diffusivity simultaneously. As anode materials for LIBs, the enhanced electrical conductivity and balanced Li⁺ diffusion significantly improve rate performance. The composite CNFs exhibit a superior capacity retention of 53.7% from 0.1 to 5 A g⁻¹, more than double of that for PAN-based CNFs. In addition, the composite CNFs present an ultra-stable cycle performance with 99.7% capacity retention at 1 A g⁻¹ even after 1000 cycles. This work demonstrates that the balance between Li⁺ diffusion and electron transport plays a key role in lithium storage performance at high current density.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been regarded as one of the most promising energy storage systems applied in portable electronics, electric vehicles, and even large-scale energy storage equipment for renewable energy [1,2]. So far, graphite and graphitized carbons are mostly employed as commercial LIBs anodes, owing to their stability and safety in long-cycle life [3,4]. However, the sluggish Li⁺ solid-state diffusion kinetics arose from the narrow interlayer distance (d_{002} , 0.335 nm) leads to a poor rate capability [5,6]. This inferior performance cannot satisfactorily meet the ever-growing demands for portable consumer electronics and electric vehicles with prolonged duration and quick charge. The intrinsic nature of materials and architecture engineering significantly influence rate performance [7,8]. Generally, anode materials are required to meet the following demands to achieve high-rate capability [7]: (1) fast solid-state diffusivity of Li⁺ (fast Li⁺ transfer); (2) high electrical conductivity (fast electron migration); (3) short diffusion length for both Li⁺ and electron; and (4)

structural stability during fast Li⁺ and electron transport. Thus, it is highly demanded for rational design strategies towards maximizing Li⁺/electron transfer and shortening transport pathways.

Nanosized carbon materials have been widely investigated as anodes for LIBs [9,10], due to their enlarged electrolyte-electrode contact area and shortened Li⁺ diffusion pathway, which exhibit both higher capacity and longer cycle life than their bulk counterparts. Amongst, the three-dimensional (3D) electrospun carbon nanofiber (CNF) film offers several unique properties [8,11–13]: (1) the nanosized structure creates abundant active sites in electrodes, contributing to an enhanced specific capacity; (2) a high surface area provided by one dimensional (1D) nanostructure effectively facilitates contact between the electrode and electrolyte, enhancing a fast charge transfer across the interface; (3) the 1D nanostructure shortens the Li⁺ diffusion length and serves as electron expressways in axial direction; (4) the interfibrillar spaces accommodate the strong volume expansion, which is structural stable for both Li⁺ and electron transport during cycling; and (5) the monolithic structure makes binders, conductive additives and current collectors

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unnecessary.

Hard carbons have shown great potential as anode materials for LIBs [14–17], with the excellent electrochemical performance and easy fabrication from biomass sources or polymers. Generally, the high proportion of sp^3 hybridized carbon in hydrocarbon precursors leads to a disordered microstructure by preventing carbon layers from reorientation during violent pyrolysis. The disordered orientation nanostructure with large amounts of micropores and expanded d_{002} results in a high capacity and fast solid-state Li^+ diffusion kinetics. However, the excessive sp^3 hybridized carbon would destroy the conjugated system of sp^2 hybridized carbon layers, which seriously impedes electrons migration [18], resulting in a deteriorated electrical conductivity and consequently an inferior rate capability [19,20]. Soft carbons, derived from hydrocarbons with high content sp^2 hybridized carbon, possess much more ordered carbon layers and high electrical conductivity (delocalized π -electron clouds exist). As a cost, the stacked carbon layers with narrowed d_{002} would inevitably sacrifice the Li^+ diffusivity. Hard-soft composite carbon materials have been proved effective for enhancing electrochemical performance, especially rate capability [21–23]. Although a series of work on this issue have been carried out [24,25], the influence of the microstructure on rate performance is still in dispute. A thorough understanding of carbon microstructure effect on the rate performance is crucial due to the emerging challenges in LIBs.

Coal tar pitch (CTP), one of the main by-products of coking industry, is a typical soft carbon precursor. Recently, CTP derived carbon materials have shown widespread potential as electrodes for energy storage and harvest, for example, alkali metal-ion batteries [19,26–29], supercapacitors [30–32], dye-sensitized solar cells [33], and CO_2 electroreduction [34], on account of their high carbon yields and excellent electrical conductivity. In the present paper, the influence of carbon microstructure on Li^+ and electron transfer has been investigated systematically by controllable introduction of CTP to polyacrylonitrile (PAN) in the electrospun carbon nanofibers (CNFs). It shows that the obtained CNF film, with CTP derived carbon clusters distributed in PAN derived hard carbon matrix provides both fast electron transport and solid-state Li^+ diffusivity. When used as anodes, the composite CNFs (PCTP9-1) present an ultra-stable cycle performance of 323 mA h g^{-1} at 1 A g^{-1} after 1000 cycles with a capacity retention 99.7%. More importantly, PCTP9-1 exhibits an enhanced capability retention of 53.7% at a current density from 0.1 to 5 A g^{-1} , more than double of that for PAN-800. This work provides a new insight into the significance of microstructure tuning on the design of high-rate carbon-based anode materials.

2. Experimental section

2.1. Electrospinning of PAN/CTP CNFs

PAN ($M_w = 150,000$) was purchased from Aldrich Chemical Co., USA. PAN was dissolved in dimethylformamide (DMF) in 10 wt%. Then a certain amount of CTP, provided by Ansteel Group Corporation, China (softening point of $70\text{ }^\circ\text{C}$), was added to the solution followed by stirring at $60\text{ }^\circ\text{C}$ for 4 h to obtain a homogeneous dark mixture. The mass ratio of PAN to CTP can be tuned as 10/0, 9/1, 7/3, and 5/5, respectively. Then the mixture was loaded into a 10 mL plastic syringe with a stainless-steel needle of 0.84 mm inner diameter. The voltage was 20 kV and distance applied to the needle to collector was 15 cm. The nanofibers were dried in a vacuum oven for 12 h to evaporate the residual solvent. Then the nanofiber films were firstly stabilized at $280\text{ }^\circ\text{C}$ in air for 2 h with a heating rate of $1\text{ }^\circ\text{C min}^{-1}$, and then carbonized at $800\text{ }^\circ\text{C}$ in N_2 for 2 h. The obtained CNFs were denoted as PAN-800, PCTP9-1, PCTP7-3, and PCTP5-5, according to the mass ratio of PAN to CTP. The fabrication procedure is illustrated in Fig. 1.

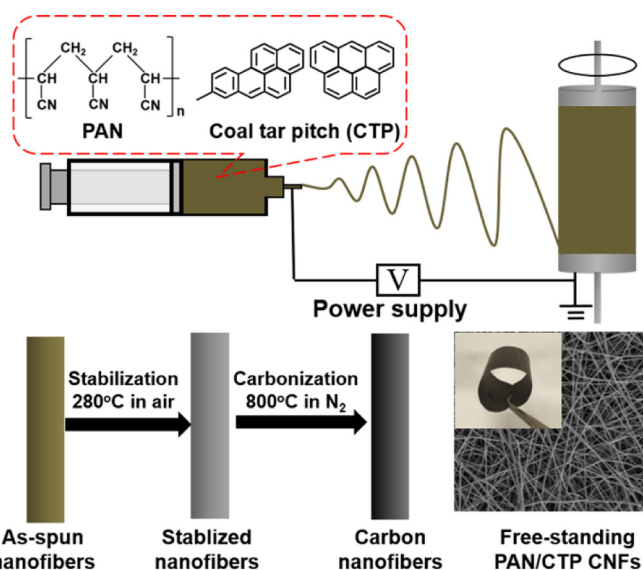


Fig. 1. Fabrication procedure of PAN/CTP CNFs.

2.2. Materials characterization

The morphology of the CNF films were examined by FE-SEM (FEI, Nova450) and HR-TEM (FEI Tecnai F30). The crystal structure was characterized on Rigaku D/Max2400 equipped with a rotating anode and a $CuK\alpha$ radiation source ($\lambda = 0.15418\text{ nm}$). Raman spectra were recorded by using a Thermo Fisher DXR Raman Microscope, using 532 nm laser excitation. Elemental analysis was measured using an elemental analyzer (Vario EL, Element). XPS analysis was studied by a Thermo ESCALAB 250XI with a monochromatic Al K X-ray source. The electrical conductivity measurements were conducted by a four-point probe method using a Keithley 2400 sourcemeter.

2.3. Electrochemical measurements

The anode slices were obtained by cutting the CNF films into disks with a diameter of 1 cm and directly employed as anodes with the absence of binders, conductive additives, and current collectors. The half cells were assembled in an Ar-filled glovebox (H_2O and O_2 below 0.1 ppm), followed by using the CNF film as LIB anodes, lithium foils as the counter/reference electrodes, polypropylene monolayer membranes as the separators, and $LiPF_6$ (1.0 mol L^{-1}) in 1:1 (v/v) mixture of EC/DEC as the electrolyte. Electrochemical impedance spectroscopy (EIS) and Cyclic voltammetry (CV) were measured on a VMP-300 electrochemical work-station over the frequency of 100 kHz to 10 mHz and a voltage window of 0.01 to 3 V vs. Li^+/Li at 0.1 mV s^{-1} , respectively. The galvanostatic charge-discharge measurements were conducted on a Land CT2001A battery testing system (Wuhan LAND electronics Co., Ltd.) at a voltage window of 0.01–3 V.

3. Results and discussion

The fabrication of PAN/CTP CNFs is shown in Fig. 1. PAN and CTP were mixed with a desired mass ratio in DMF, yielding a homogenous dark suspension. Then the electrospinning was carried out by a home-built apparatus to obtain dark brown carbon nanofiber films. After stabilization and carbonization, the CNF films maintain excellent integrity and flexibility, which is advantageous to the applications of flexible and wearable energy storage devices. Then the CNF films were cut into disks with a diameter of 1 cm (thickness: $\sim 140\text{ }\mu\text{m}$, surface density: $\sim 1.3\text{ mg cm}^{-2}$). As shown in Fig. 2a and b, PCTP9-1 exhibits randomly 3D interconnected network composed of uniform and continuous CNFs with diameters ranging between 300 and 350 nm, which

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