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Carboxyl functionalized carbon fibers with preserved tensile strength and electrochemical performance used as anodes of structural lithium-ion batteries

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ABSTRACT

Carboxyl functionalized carbon fibers with preserved tensile strength and electrochemical properties were acquired through a simple chemical oxidation method, and the proposed underlying mechanism was verified. The surface of carboxyl functionalizing carbon fibers is necessary in acquiring functional groups on the surface of carbon fibers to further improve the thermal, electrical or mechanical properties of the fibers. Functionalization should preserve the tensile strength and electrochemical properties of carbon fibers, because the anodes of structural batteries need to have high strength and electrochemical properties. Functionalized with mixed H_2SO_4/HNO_3 considerably reduced the tensile strength of carbon fibers. By contrast, the appearance of H_3PO_4 preserved the tensile strength of functionalized carbon fibers, reduced the dispersion level of tensile strength values, and effectively increased the concentration of functional acid groups on the surface of carbon fibers. The presence of phosphoric acid hindered the over-oxidation of turbostratic carbon, and consequently preserved the tensile strength of carbon fibers. The increased proportion of turbostratic carbon on the surface of carbon fibers concurrently enhanced the electrochemical properties of carbon fibers.

1. Introduction

The use of structural batteries could effectively decrease the whole mass of devices by acting as integrated load-carrying parts (e.g., car roof) [1–3]. By combining electrochemical and mechanical properties in the same material, a structural battery could function both as a structural element and as energy storage, having the possibility to become a fully integrated part of a device. In addition, the power and energy density could be increased on a system level. Carbon fiber (CF) is a promising lightweight material used as electrode material in structural power batteries because of its high specific tensile properties and carbonaceous microstructure, which enables reversible lithium-intercalation reactions [4–6]. However, CF used in lithium-ion batteries display poor capacity, only about 100 mAh g^{-1} at moderate lithiation rates [7]. Moreover, surfaces are chemically inert and manifest weak interfacial interactions [8]. Therefore CF cannot be easily used to form composites with high-capacity materials (e.g. silicon [9], $ZnCo_2O_4$ [10] and WO_3 [11]) to effectively improve electrical properties [12,13], and there is poor interfacial strength between CF and solid polymer electrolytes [14–16]. Therefore the surface carboxyl functionalization of pristine carbon fibers is necessary.

There are a number of existing functionalization methods are studied to address different application requirements of functionalizing carbon fibers, but there are few is aimed at carbon fibers as structure electrode material. Different with the other application requirements, carbon fibers used as structure electrode material have a high demands on both tensile strength and electrochemical properties. Hence the appropriate functionalization method is necessary and urgently needed. In this study, chemical oxidation method is improved to address the high demands for carbon fibers as structure electrode materials because of the following reasons. First, compared with other functional groups, carboxyl groups are proved more suitable for adhesion with nanoparticles [12], the addition of surface polar functional groups effectively increases surface wettability of fibers, and the chemical oxidation using strong oxidizing acids is easier to obtain more carboxyl groups than the others [17]. Second, chemical oxidation method is simpler and cost less, and has less potential to damage elec-

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trochemical properties. Third, although surface functional group grafting procedures could preserve tensile strength of CF [18,19], grafting reactions using solid organic matters as secondary materials have great potential to damage electrode electrical properties. Besides, grafting reactions using carbon nanotube (CNT) [20], carbon aerogel or graphene as a secondary material suffer high cost and low productive efficiency on the synthesis of CNT or graphene and grafting processes.

However, chemical oxidation is usually accompanied by the cleavage of C—C bond, and creates surface defects, which are undesirable for fiber tensile strength, and cannot be ignored. The negative effect of chemical oxidation method should be decreased. Otherwise, the application of carbon fibers would be influenced. A previous study indicated that the use of phosphoric acid as secondary acid can protect the vicinal diols by forming a cyclic structure, thereby preventing or retarding the over-oxidation of the CNT and nanoribbon [21]. Therefore, the presence of phosphoric acid may be used to prevent C—C from breaking. Meanwhile the tensile strength of carbon fibers is determined by the turbostratic structure. Hence, we hypothesize that the addition of phosphoric acid could preserve the strength of carbon fibers.

In this study, we developed a carboxyl functionalization method with mixed phosphoric/sulfuric/nitric acids ($H_3PO_4/H_2SO_4/HNO_3$) for carbon fiber surface. The effectiveness of this proposed method on increasing the concentration of surface acid functional groups, tensile strength and electrochemical properties of carbon fibers was assessed. The proposed functionalization mechanism was also verified by several tests. The PAN-based T800 carbon fibers were viewed as a highly promising structural electrode material and have a promising prospect in further researching during the process of developing a functional structural battery in the previous study [22]. Hence PAN-based T800 carbon fibers are utilized in this study.

2. Experimental

PAN-based carbon fibers were coated particularly with epoxy or polyurethane resin. PAN-based T800 carbon fibers were desized through solvent extraction using a superfluous volume of acetone for 72 h at room temperature to avoid the influence of surface resin on tensile strength and electrochemical properties especially the reversible capacity. The desized carbon fiber (DCF), was considered as the unmodified carbon fiber. The carbon fibers were then filtered and dried at 60 °C for 12 h to remove excess acetone. The two kinds of mixed acids used for carbon fiber functionalization include mixed HNO_3/H_2SO_4 ($V_{HNO3}:V_{H2SO4} = 1:3$) which is a promising solvent for carboxyl functionalization [8], and mixed $H_3PO_4/HNO_3/H_2SO_4$ ($V_{H3PO4}:V_{HNO3}:V_{H2SO4} = 1:3:9$). The carbon fibers were functionalized at 60 °C at precisely controlled times between 0.25 and 6 h. In a typical reaction, each bunch of 1.2-m-long carbon fibers was added to 30 ml of the acid mixture in a reaction flask. Each bunch of carbon fiber contains 12k single-filament carbon fibers. The functionalized carbon fibers were washed with deionized water, until the pH of the supernatant fluid was adjusted to ~7. The fibers were subsequently washed and sonication for 5 min the fibers were then washed again until the pH reached ~7. To remove the adsorbed H_2SO_4, HNO_3 and H_3PO_4 from the carbon fiber surface, while preserving directly bonded S, N and acidic oxygen-containing functional groups. The sample numbers and corresponding functionalization conditions are shown in Table 1. All chemicals including H_2SO_4 (98 wt%), HNO_3 (67 wt%), H_3PO_4 (98 wt%), HCl (37 wt%), acetone, and $NaHCO_3$ were used without further purification. HNO_3, H_2SO_4 and H_3PO_4 were used without dilution.

Table 1
Summary of functionalization conditions and numbers.

Number	Acid	Time/h
1	None	0
2	$HNO_3/H_2SO_4 = 1:3$	0.25
3	$HNO_3/H_2SO_4 = 1:3$	0.5
4	$HNO_3/H_2SO_4 = 1:3$	1
5	$HNO_3/H_2SO_4 = 1:3$	2
6	$HNO_3/H_2SO_4 = 1:3$	4
7	$HNO_3/H_2SO_4 = 1:3$	6
8	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	0.25
9	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	0.5
10	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	1
11	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	2
12	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	4
13	$H_3PO_4/HNO_3/H_2SO_4 = 1:3:9$	6

The tensile strength of single-filament carbon fibers was tested in according to BS ISO 11566:1996 [24]. Epoxy resins were employed as adhesive. The samples were placed in an oven at 90 °C for 12 h to ensure that carbon fibers were fixed well. The single fiber tensile strength was measured using a Single Fiber Electronic Tensile Strength Tester at a loading speed of 2 mm min^{-1}. At least 20 valid data for each condition were acquired. The cross-sectional area of the specimens was calculated using the average diameter (5.3 μm) which is measured by scanning electron microscopy (SEM) analysis. The average of at least 200 valid data from different regions was calculated to ensure the accuracy of the results.

Titration was conducted to evaluate the concentration of acidic functional groups. In a typical reaction, carbon fibers were placed in reaction flasks, and added with 50 ml of 0.1 M $NaHCO_3$ solution. The flasks were then placed on a shaking table for 24 h at 25 °C, to ensure that all the acidic polar functional groups participated in the reaction with $NaHCO_3$. Subsequently, 20 ml of the supernatant liquid was poured in a dried cleaned flask and titrated with 0.1 M HCl solution to the end point. The consumption of HCl solution was recorded. Each kind of fibers was titrated four times, and the average of the results was obtained.

Electrochemical performance was assessed using a CR2032-type coin cell (MTI, America). Carbon fibers, acetylene black and polyvinylidene difluoride were mixed at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidine. The mixed slurry was pressed onto a copper foil, used as working electrode and dried at 90 °C for 24 h. The lithium foil was used as counter electrodes and reference electrodes. The galvanostatic charge–discharge performance was evaluated within the voltage range from 0.005 to 3.0 V (versus Li/Li^+) at a constant current of 20 mA g^{-1} on a LAND CT2001A test system at room temperature. The galvanostatic charge–discharge performance carried out in a constant current of 100 mA g^{-1} was compared with that in literature. Galvanostatic measurements at current density ranging from 50 mA/g (~0.13C) to 350 mA/g (~0.93C) were performed to acquire the rate capacity and capacity of carbon fibers at high current rate. Electrochemical impedance spectroscopy (EIS) analysis was performed within the frequency range from 100 kHz to 10 mHz at a sweep rate of 5 mV s^{-1} and open circuit potential (OCP). Cyclic voltammetry (CV) test was accomplished within the voltage range of 0.005–3 V at a sweep rate of 0.5 mV s^{-1}. Both procedures were carried out on a CH instrument CHI620D electrochemical station.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250 (Thermo Fisher Scientific, USA) with a monochromatic Al Kα source (1486.6 eV), at a base pressure of 2×10^{-9} mbar. High-resolution spectra were obtained at a perpendicular take-off angle by using pass energy of 25 eV and 0.05 eV energy steps. The species and percentage of surface atoms in the titrated functionalized carbon fibers were detected using X-ray energy dispersive spectrometer (EDS) with an acceleration volt-