Biotechnology humic acids-based electrospun carbon nanofibers as cost-efficient electrodes for lithium-ion batteries

Pin-Yi Zhao ^{a,b}, Yan Guo ^{a,b}, Bao-Jun Yu ^{a,b}, Jie Zhang ^{a,b}, Cheng-Yang Wang ^{a,b,*}

^a *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China*

^b *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China*

*Corresponding author. Tel/fax: +86 22 27890481;

E-mail address: cywang@tju.edu.cn (C.Y. Wang)

ABSTRACT:

Bio-based, cost-effective carbon nanofibers are fabricated from polyacrylonitrile (PAN) – refined biotechnology humic acids (RB) via simple eletrospinning after stabilization and carbonization. The influence of PAN/ RB mass ratios and heat-treatment temperatures (HTTs) on structure and morphology is systematically studied. Excitingly, a first discharge/charge capacity of 937.9/613.4 mAh g⁻¹(coulombic efficiency of 65.4%) is achieved at 20 mA g⁻¹ for PB7/3-800 in lithium-ion batteries (LIBs). Meanwhile, a charge capacity of 348.2 mAh g⁻¹ (about 89% retention ratio) remains even after 100 cycles at 0.1 A g⁻¹. It is demonstrated that biomass humic acids can be applied as a promising precursor to fabricate high performance, low-cost, as well as “green” carbon electrode material for LIBs.

Keywords: Biotechnology humic acids; Carbon nanofibers; Electrospinning; Lithium-ion batteries

1. Introduction

Over the years, an ever-growing concentration on portable electronic devices has witnessed the application of LIBs in electronic industries. Benefited from high energy density and extended cycle lifetime, LIBs are now anticipated to be applied in electric vehicles and renewable energy storage systems [1–4]. It is well acknowledged that a high reversible anode is essential for efficient and industrial applications of LIBs. Different types of carbonaceous materials, such as carbon spheres [5], carbon black [6], porous carbon [7–8], and carbon fibers [9–10] have served as primary anode materials

for LIBs. Nevertheless, subjected to severe scarcity of resources and various environmental issues, it is still an austere challenge to develop mechanically flexible electrode materials which combine merits of high electrochemical performance with low cost for its wider applications.

Screening “green” and economically feasible precursor as well as smart synthesis routine can be an effective methodology to solve the issue above. Based on renewable biomass materials, carbon nanofibers display an attractive prospect as an electrode material with noticeable environmental and capital benefits [11]. Formed from microbial decomposition of animal and plant residues, widely distributed in soils, sediments, and natural waters, humic acids (HAs) feature such superiorities as abundance, low cost, “green”, and no-toxicity with more than 40 wt % carbon composition [12–13]. During the past decades, humic acids were frequently used in the evaluation of natural organic matters as well as transportation of metal oxide nanoparticles [14]. While lignin-based electrospun carbon nanofibers (ECNFs) have been fabricated through stabilization and carbonization [15], during which renewable biomass have been converted to ECNFs as battery electrodes [16–18], little attention has been paid to humic acids, a decomposition product of lignin [12] for its low-cost, environmentally friendly superiorities as potential electrode materials.

Actuated by electrostatic forces, electrospinning is serving as a convenient, low-cost and quantitative technique for the production of nanofibers [19]. The industrialization of inexpensive electrospun nanofibers (ENFs) is strongly dependent on

improvements of the technique. Electrode materials of different morphologies can be easily prepared by adjusting solution properties to processing parameters [16, 18, 20–22]. Costs of electrode fabrication are reduced by introduction of a round collector and multi-needle spinneret, while greatly enhancing the productivity of nanofibers. Finally, without metal current collectors or auxiliary additives, ENFs are often fabricated in a “web” form, which are precursors of flexible freestanding electrodes [23]. This character not only contributes to cost reduction by simplifying cell packing process, but also lower inactive weight, thus improving power density and volumetric energy [24–25]. Therefore, eletrospinning is quite promising as an economically feasible technology for industrialization of battery electrodes in the future. However, little research has been done for its application in LIBs [23–24].

In this paper, 3D interconnected mechanically flexible polyacrylonitrile (PAN)/RB-carbon nanofibers (PB-CNFs) are prepared by plain electrospinning, followed by thermal treatment which involves carbonization after stabilization. In order to improve viscosity and spinnability, PAN is introduced in the RB solution [22], while abundant and low-cost biotechnology humic acids, as an environmentally friendly bio-based precursor, is expected to reduce the cost of carbon nanofibers. The influence of RB content and heat-treatment temperatures (HTTs) on morphology and structure of PB-CNFs, are systemically examined. As anodes for LIBs without a binder or current collector, their electrochemical properties are intensively clarified for the first time.

2. Experimental

2.1. Fabrication of carbon nanofibers

Before electrospinning, salts and ashes in the biotechnology humic acids (Beijing Zimingyuan Co., Ltd) were thoroughly removed, leaving the refined biotechnology humic acids (referred to as “RB” in the following text). To prepare PAN (Mw=80000, Aldrich Co.) / RB blends with mass ratios of 9/1, 8/2, and 7/3, 12 wt % PAN was first dissolved in 88 wt % N, N-dimethylform amide (DMF) solvents, then corresponding amounts of RB were added into each PAN-DMF solution at 50 °C under continuous stirring [26]. After natural cooling to room temperature, the solution was transferred to a 5 ml syringe in a syringe pump. The flow rate was maintained at 1 mL h⁻¹. The needle tip-to-plate substrate distance was set as 20 cm with two high voltages of +20 kV and -5.00 kV, respectively. The PAN / RB composite nanofibers were collected as overlaid mats on aluminum foil which covered the plate and dried at 60 °C under vacuum overnight.

The dried nanofibrous mats were stabilized at 250 °C for 1 h in a tube furnace with air. Thereafter, they were carbonized at various HTTs (see Table 1) for 0.5 h in N₂ atmosphere. The fabricated PB-CNFs, denoted as PB9/1-800, PB9/1-1000, PB9/1-1300, PB8/2-800, PB8/2-1000, PB8/2-1300, PB7/3-800, PB7/3-1000, and PB7/3-1300, as summarized in Table 1, were prepared.

2.2. Material characterizations

X-ray diffraction (XRD) patterns were acquired from a Rigaku D/Max 2500 X-ray diffractometer operated at 40 kV and 90 mA using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$).

The structure parameters including the interlayer distance d_{002} and crystallite size: the c-axis length (L_c) were calculated by XRD spectra using the Bragg and Scherrer equations. Brunauere Emmette Teller (BET) specific surface areas were determined by N_2 adsorption at 77 K on Micromeritics Analytical Services (TriStar 3000, GA). Field emission scanning electron microscopy (FESEM, Nano430) and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai G2 F20) were operated to examine the morphology and microstructure of the fibers.

2.3. Electrochemical measurement

The PB-CNFs were directly used as working electrodes without adding any polymeric binder or conductive additive. The mass loading of active material was in the range of 2–3 mg cm⁻². After drying in a vacuum oven at 120 °C overnight, LIBs were assembled with lithium plate as both the counter electrode and reference electrode and operated within a potential range of 0–2.5 V. The electrolyte used was 1 M LiPF₆ solution in a 1:1 (V:V) mixture of ethylene carbonate and dimethyl carbonate. Galvanostatic charge–discharge experiments were conducted using a multichannel Land Battery Test System. Cyclic voltammetry (CV) testing at a scan rate of 0.1 mV s⁻¹ was performed on a CHI604a electrochemical workstation (Chenhua Instrument Company, Shanghai, China).

3. Results and discussion

3.1. Characterizations of morphology and structure

As a consequence of low molecular weight, high polydispersity, and deficient in

chain structures or molecular entanglements, a single RB solution couldn't be electrospun into nanofibers at any RB concentration. So under this circumstance, for sakes of fluid properties and electrospinnability, spinning auxiliaries are essential. PAN is renowned to produce carbon nanofibers with excellent mechanical strength from 10-12 wt % PAN-DMF solution [20, 27]. Mixtures containing various PAN/ RB weight ratios of 9/1, 8/2, and 7/3 can be electrospun by improved viscosity and spinnability. Unfortunately, RB weight ratios higher than 30% would end up in electrospin failure as a result of over-viscous solutions and poor rheological property [26]. In other words, precursors with RB content higher than 30 wt % could not be electrospun.

The morphologies of electrospun nanofibers with varied compositions are shown in Fig. 1a₀, b₀, c₀. All nanofibers exhibit a long and smooth fibrous morphology with average diameters increasing from around 150 nm at 10 wt % RB to 300 nm at 30 wt % RB. The diameters of the nanofibers become larger with an increase in RB ratios, which is also positively correlated with both concentrations and viscosities of the polymer solutions. After stabilization and carbonization, as a result of gas evolution (e.g., CO₂, H₂O, NH₃) during thermal decomposition, the diameters of PB-CNFs become smaller accompanied with a large weight loss [27]. Under HTTs of 800, 1000, and 1300 °C, a small difference is observed in terms of fiber size, while no phenomenal variations in macromorphology (Fig. 1a₁–a₃, or b₁–b₃, or c₁–c₃) can be detected. This kind of interconnected conductive 3-D network structure is considered

suitable for fast ionic and electronic transport [9].

Fig. 2 shows HRTEM images of different PB-CNFs. With an increased amount of RB in the solution, there is no evident long-range structural variation in the precursor nanofibers, as is shown in the figures of PB9/1-1000, PB8/2-1000, PB7/3-1000 (Fig. 2 a₁, b₁, c₁). At the same time, turbostratic graphitic microstructures of hard carbon materials can be seen, and interpreted with the falling cards model [28]. However, different short-range structures, especially for PB-CNFs-1000 and PB-CNFs-1300, can be observed. Less contacted graphite-like micro-crystallites constructed by several short-range parallel graphene sheets are shown in PB-CNFs with higher RB contents. Furthermore, as the content of RB increases, the distance between parallel graphene sheets turns more significant while the size of micro-crystallites become tinier, revealing more disordered short-range structures. As is illustrated in the figure (Fig. 2a₁–a₃, or b₁–b₃, or c₁–c₃), matrix graphitization degree increases with an elevation of HTTs. In addition, the layer shift and fold indicate favorable sites for lithium insertion and extraction, yielding the appearance of some better pore connectivity and micropores.

XRD patterns are obtained to further characterize the microstructures of PB-CNFs, as is shown in Fig. 3. The results of the XRD analysis are presented in Table 2, together with the results of BET. There are two broad diffraction peaks located at around 24° and 43°, which could be ascribed to the crystallographic planes of (002) and (100) [29]. As is illuminated in Table 2, with an augment in the mass ratios of RB to PAN, the average

interplanar spacing of d_{002} increases, signifying that the introduction of RB bring about a large amount of structural disorder and topological defects to the PB-CNFs [30]. The wider interlayer spacing promotes lithium ion transport and storage among graphene layers. The crystallite size along the c-axis (L_c) and the size of graphene planes (L_a) are calculated using the Scherrer formula [31]. With the increase of HTTs from 800 to 1300 °C, d_{002} of three PB7/3-CNFs samples declines from 4.45 to 4.33 Å, accompanied with the enhancement of L_c , exhibiting a noticeable increase in structural order [32].

In addition, with the increase of RB content in the precursors, the BET surface areas drop slightly as shown in Table 2. This phenomenon may be attributed to higher RB contents leading to larger diameters in the carbon nanofibers [15]. This tendency in BET surface areas is quite unnoticeable, so it can be inferred that although the elevation of RB content does lead to a more defective structure, it becomes less influential in the fluctuant pore structure. The small difference and low surface area in the pore structure between PB-CNFs with various RB contents may play an inferior role in their corresponded electrochemical behaviors. One change of importance is the emergence of extended peak tails in the low Bragg region when HTT is slowly elevated to 1300 °C (Fig. 3), which indicates heat treatment at higher temperature can give rise to the generation of nanosized pores [33]. Besides, it is demonstrated in the BET measurements (Table 2) that, with the improvement of HTTs, due to the fact that some macropores and mesopores are transformed into micropores [34], there is a subsequent increase in the surface areas of carbon nanofibers, which coincides with XRD results.

3.2. Electrochemical characterization

The galvanostatic charge–discharge experiments of samples with diverse parameters are proceeded to comparatively understand the impact of material structure on lithium ions deintercalation and intercalation processes. All galvanostatic charge–discharge cycling are conducted at a current density of 20 mA g^{-1} between 0.01 and 2.5 V. As is displayed in Fig.4, PB-CNFs anodes with identical HTTs but different RB contents exhibit similar voltage profiles, except for a slight increased capacity positively related with RB contents during the 1st cycle. For instance, the charge capacities of PB9/1-800, PB8/2-800, and PB7/3-800 are 580.3, 598.7 and 613.4, respectively. These tiny alternations in the values can be interpreted as variations in graphene layers and microstructures [29]. For one reason, with higher RB contents, there are larger graphene layers of PB-CNFs between which lithium ions can insert, thus leading to a higher capacity. For another reason, induced by an increased RB amount, a more disordered carbon structure and topological defects facilitate lithium intercalation/absorption. Therefore, the samples with 30% RB were selected for the subsequent electrochemical measurements. In sharp contrast, HTTs have strong impacts on specific capacities as well as the shape of voltage curves.

The discharge capacities of the samples with 30% RB at different HTTs are shown in Fig 5a. Plateau capacity is the fraction of the total capacity associated with the plateau below 0.1 V whereas sloping capacity is the fraction of the total capacity associated with the slope above 0.1 V [35]. As is anticipated for carbonaceous materials

processed at low HTTs, due to a poor and closed porous structure, anodes with a carbonization temperature of 800 °C display only a precipitous slope with small low-voltage plateau, which is in accordance with their comparatively low BET surface areas (see Table 2), making it quite difficult for previous intercalated lithium to extract. With an escalation in the carbonization temperature, a capacity plateau can be noticed at the low voltage region [36–37], which can be elucidated by a decrease in intercalation sites, such as basal surface, edges, interactions between heteroelements and lithium ions. The micropore in PB-CNFs-1000 can supply efficient sites for Li extraction and insertion, thus bringing about gradually flatter plateaus. Therefore, combined with BET data in table 2 and a decreased plateau capacity at higher HTTs, it is deduced that major intercalants are solvated lithium ions, and macropores in PB-CNFs-1300 have no facilitation in removing solvent molecules from solvated lithium ions, which has no influence in plateau capacity.

As is illustrated in Table 2, among all the samples, PB7/3-800 exhibits the highest reversible capacity of 613.4 mAh g⁻¹ but a relatively low initial coulombic efficiency of 65.4 %. Compared with samples of low HTTs, the first coulombic efficiencies of PB-CNFs with high HTTs are substantially enhanced. Primarily attributed to the formation of a solid electrolyte interface (SEI) layer from decomposition of electrolyte, low initial coulombic efficiencies are consequent result of some irreversible insertion reactions in the adjacent areas of remanent heteroatom atoms as well as some immanent voids or sites [38]. For certain carbon electrode materials, a considerable method to

improve first coulombic efficiencies is to increase heat-treatment temperatures (HTTs) [39]. The carbonization process accelerates as HTTs increase, therefore graphite-like micro-crystallites grow up. Meanwhile, N, H and O elements are eliminated in forms of volatile gases. Less "edge" carbon and defective graphitic structures, along with lower heteroatom content cut down irreversible reactions, thus reducing capacity loss.

To understand the mechanisms in more details, CV experiments are conducted on the electrode of PB7/3-800. CV curves in the first three cycles at a scan rate of 0.1 mV s^{-1} between 0 and 2.5 V are shown in Fig. 5b. During the first discharge process, an irreversible cathodic peak appears at 0.8 V versus Li/Li^+ , corresponding to the formation of the SEI layer [40]. As is demonstrated in the voltage range from 0.1 V to 1.5 V (vs Li^+/Li), the apparent reduction peak is the result of reversible intercalation of lithium ions among graphene layers [41], consistent with the outcomes from the galvanostatic charge/discharge data. The following CV curves almost overlap, indicating the capacity attenuation mainly emerging in the first cycle. In other words, stable lithium ion insertion-extraction mechanisms are performed during subsequent cycles.

All results and discussions above indicate that: graphitization degree, porous textures and microstructure dramatically impact on capacity during the process of intercalation and deintercalation of lithium ions [39, 42–43].

Aimed to verify the impacts of HTTs on electrochemical performances, rate capability and the cycling life of samples with 30 wt % RB content at different HTTs

are further investigated in details. Rate performance is conducted under current densities from 37.2 mA g^{-1} to 1860 mA g^{-1} and cycle performance is tested under the current density of 100 mA g^{-1} . Results of the rate capability are displayed in Fig. 6a. With an increase in HTT, the percentage of capacity retention rises which may be mainly contributed by a higher electric conductivity and the increase of graphite-like crystallite. Particularly, PB7/3-1300 displays an outstanding rate performance. However, the specific capacities are relatively low. For example, only 150 mAh g^{-1} reversible capacity can be achieved at 372 mA g^{-1} . As for PB7/3-800, the specific capacities are much higher in various current densities than other electrodes. However, overall rate capabilities are not that good. It is well acknowledged that in most situations for LIBs, rate capabilities are dependent on porous structure and electronic conductivity of electrode materials [7, 35, 44]. These characters are strongly linked with the intrinsic microstructure and heat treatment process. The pore structure of PB7/3-800 is not sufficiently developed for ion transportation, which hinders its rate capability. In addition, during large current operations, a declined intergraphene space and tinier pore size are not conducive to the retention of electrochemical capacity [39]. In short, better rate capability can be achieved by optimizing heat treatment process (such as heating rate, holding time or HTT) and seeking a preferable relationship in terms of pore structure, intergraphene spacing and electric conductivity for PB-CNFs electrodes. These limited parameters of the rate capability call for more experimental research among diverse electrode materials and more efforts can be made to develop rate

capability by microstructural control and material modification.

It is expected that good mechanical properties and unique fibrous structure of free-standing electrodes are conducive to good cycling performances. Fig. 6b shows the cycle performances of the PB7/3 electrodes at 100 mA g^{-1} under three HTTs. The carbonization temperature does not exert a substantial influence on the cycling performance. For PB7/3-800, the electrode is stabilized at a capacity of 348.2 mAh g^{-1} after 100 cycles, corresponding to a capacity retention ratio of 89%. As is mentioned above, PB-CNFs electrodes have relatively low initial coulombic efficiencies. But in cycling performances, electrodes can reach over 99% charge/discharge ratio after few cycles, implying an admirable reversibility of insertion/extraction in the PB-CNFs, which is explained by structural stability. These results demonstrate that RB-mixing is a successful approach to improve the electrochemical performance.

To authenticate structure changes of the electrode after cycling, and propose an insightful mechanism for the good cycling stability in the future, the as-tested electrode in Fig.6b is disassembled after 100 cycles. Fig.7a shows the after-cycled digital image of the PB7/3-1300 electrode. An excellent structural stability is verified, as original size, shape, and structural integrity, still remain. SEM characterization is conducted on the cycled electrode. The SEM images in Fig. 7b exhibit that with a similar diameter and no obvious fracture or pulverization, the carbon fibers still maintain a continuous, long, and robust morphology, signifying a favorable electrochemical stability of the material. It can be assumed that mechanical stress caused by lithium-ion insertion/extraction is

counteracted by suitable pore and large interlayer spacing of carbon fibers. At the same time, electrodes on which a stable and compact SEI film evenly distributes with a rough external appearance, reduce the cointercalation of solvent molecular thus improving the cycle performance.

4. Conclusion

Low-cost and free-standing carbon fibers have been prepared from PAN and RB via electrospinning followed by thermal annealing. . With an increase in HTT and RB / PAN mass ratios, various microporous structures can be obtained. After comparisons of electrochemical performances and discussions on mechanisms, the PB7/3-800 sample shows the best comprehensive performance, exhibiting a high initial efficiency of 65.4% at a current density of 20 mA g⁻¹ and outstanding electrochemical stability with a capacity of 348.2 mAh g⁻¹ after 100 cycles. As a result, these PB-CNFs manifest superior electrochemical performance when evaluated as electrode materials for LIBs. These excellent performances, in addition to its inexpensive as well as “green” precursor sources and economical synthesis routines, make carbonized PAN/ RB a sustainable electrode material for LIBs.

Acknowledgements

This research is supported by the National High Technology Research and Development Program of China (863) (2013AA050905, 2014AA052301), the National Nature Science Foundation of China (51172160, 50902102) and NSF of Tianjin City (11JCYBJC07500).

References

- [1] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J.C. Gonzalez, T. Rojo, *Energ Environ. Sci.* 5 (2012) 5884–5901.
- [2] M.D. Slater, D. Kim, E. Lee, C. S. Johnson, *Adv. Funct. Mater.* 8 (2013) 947–958.
- [3] Y. Matsuo, K. Ueda, *J. Power Sources.* 263 (2014) 158–162.
- [4] H.L. Pan, Y.S. Hu, L.Q. Chen, *Energ. Environ. Sci.* 6 (2013) 2338–2360.
- [5] K. Tang, L. Fu, R.J. White, L. Yu, M.M. Titirici, M. Antonietti, J. Maier, *Adv. Energy Mater.* 2 (2012) 873–877.
- [6] R. Alcantara, J.M. J-Mateos, P. Lavela, J.L. Tirado, *J. Electrochem. Commun.* 3 (2001) 639–642.
- [7] S. Wenzel, T. Hara, J. Janek, P. Adelhelm, *Energ Environ. Sci.* 4 (2011) 3342–3344.
- [8] Y.Y. Hu, Z.Y. Wen, X.W. Wu, J. Jin, *J. Power Sources.* 219 (2012) 1–8.
- [9] T.Q. Chen, Y. Liu, L. Pan, T. Lu, Y. Yao, Z. Sun, D.H.C. Chua, Q. Chen, *J. Mater. Chem. A.* 2 (2014) 4117–4121.
- [10] Z.H. Wang, L. Qie, L.X. Yuan, W.X. Zhang, X.L. Hu, Y.H. Huang, *Carbon.* 55 (2013) 328–334.
- [11] X. Li, W. Xing, S.P. Zhuo, J. Zhou, F. Li, S.Z. Qiao, G.Q. Lu, *Bioresour. Technol.* 102 (2011) 1118–1123.
- [12] F. J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions*, second ed., Wiley, New York, 1994.
- [13] T. Jiang, G.H. Han, Y. B. Zhang, G. H. Li, Y. F. Huang, *Int. J. Miner. Process.* 100

- (2011) 172–178.
- [14] Y. L. Zhou, Y. B. Zhang, P. Li, G. H. Li, T. Jiang, *Powder Technology*. 251 (2014) 1–8.
- [15] D.I. Choi, J.N. Lee, J.C. Song, P.H. Kang, J.K. Park, Y.M. Lee, *J Solid State Electrochem*. 17 (2013) 2471–2475.
- [16] Y.J. Zhu, X.G. Han, Y.H. Xu, Y.H. Liu, S.Y. Zheng, K. Xu, L.B. Hu, C.S. Wang, *ACS Nano*. 7 (2013) 6378–6386.
- [17] B-H. Kim, K.S. Yang, Y. A. Kim, Y.J. Kim, B. An, K. Oshida, *J. Power Sources*. 196 (2011) 10496–10501.
- [18] W.H. Li, L.C. Zeng, Z.Z. Yang, L. Gu, J.Q. Wang, X.W. Liu, J.X. Cheng, Y. Yu, *Nanoscale*. 6 (2014) 693–698.
- [19] Li D, Xia Y, *Adv. Mater*. 16(2004) 1151–1170.
- [20] C. Kim, K.S. Yang, M. Kojima, K. Yoshida, Y.J. Kim, Y.A. Kim, M. Endo, *Adv. Funct. Mater*. 16(2006) 2393–2397.
- [21] Y.Z. Wu, M.V. Reddy, B.V.R. Chowdari, S. Ramakrishna, *ACS Appl. Mater. Interfaces*. 5(2013) 12175–12184.
- [22] C.L. Lai, Z.P. Zhou, L.F. Zhang, X.X. Wang, Q.X. Zhou, Y. Zhao, Y.C. Wang, X.F. Wu, Z.T. Zhu, H. Fong, *J. Power Sources*. 247(2014) 134–141.
- [23] L. Wu, X.H. Hu, J.F. Qian, F. Pei, F.Y. Wu, R.J. Mao, X.P. Ai, H.X. Yang, Y.L. Cao, *Energ Environ. Sci*. 7(2014) 323–328.
- [24] H.Y. Wang, P. Gao, S.F. Lu, H.D. Liu, G. Yang, J. Pinto, X.F. Jiang, *Electrochim.*

- Acta. 58(2011) 44–51.
- [25] L. Qie, W.M. Chen, Z.H. Wang, Q.G. Shao, X. Li, L.X. Yuan, X.L. Hu, W.X. Zhang, Y.H. Huang, *Adv. Mater.* 24(2012) 2047–2050.
- [26] J. Jin, B.J. Yu, Z.Q. Shi, C.Y. Wang, C.B. Chong, *J. Power Sources.* 272 (2014) 800–807.
- [27] J.C. Chen, I.R. Harrison, *Carbon.* 40 (2002) 25–45.
- [28] P. Thomas, D. Billaud, *Electrochim. Acta.* 47 (2002) 3303–3307.
- [29] J. Wang, J.L. Liu, Y.G. Wang, C.X. Wang, *Electrochim. Acta.* 74 (2012) 1–7.
- [30] B.-J. Kim, S.-J. Park, *J. Colloid Interface Sci.* 315 (2007) 791–794.
- [31] J. Biscoe, B.E. Warren, *J. Appl. Phys.* 13 (1942) 364–371.
- [32] Z.P. Zhou, C.L. Lai, L.F. Zhang, Y. Qian, H.Q. Hou, D.H. Reneker, H. Fong, *Polymer.* 50 (2009) 2999–3006.
- [33] A. Gibaud, J.S. Xue, J.R. Dahn, *Carbon.* 34 (1996) 499–503.
- [34] Y. Guo, Z.Q. Shi, M.M. Chen, C.Y. Wang, *J. Power Sources.* 252 (2014) 235–243.
- [35] J. Ding, H.L. Wang, Z. Li, A. Kohandehghan, K. Cui, Z.W. Xu, B. Zahiri, X.H. Tan, E.M. Lotfabad, B.C. Olsen, D. Mitlin, *ACS Nano.* 7 (2013) 11004–11015.
- [36] D.A. Stevens, J.R. Dahn, *J. Electrochem. Soc.* 147 (2000) 1271–1273.
- [37] K. Gotoh, T. Ishikawa, S. Shimadzu, N. Yabuuchi, S. Komaba, K. Takeda, A. Goto, K. Deguchi, S. Ohki, K. Hashi, T. Shimizu, H. Ishida, *J. Power Sources.* 225 (2013) 137–140.
- [38] Y.L. Cao, L.F. Xiao, M.L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z.M. Nie,

- L.V. Saraf, Z.G. Yang, J. Liu, Nano Letters. 12 (2012) 3783–3787.
- [39] J. Jin, Z.Q. Shi, C.Y. Cheng, Solid State Ionics. 261(2014) 5–10.
- [40] Y.L. Cao, L.F. Xiao, X.P. Ai, H.X. Yang, Electrochem. Solid-State Lett, 6 (2003) A30–33.
- [41] R. Alcantara, P. Lavela, G.F. Ortiz, J.L. Tirado, Electrochem. Solid-State Lett. 8 (2005) A222–225.
- [42] H.S. Zhou, S.M. Zhu, M. Hibino, I. Honma, M. Ichihara, Adv. Mater. 15 (2003) 2107–2111.
- [43] J.F. Ni, Y.Y. Huang, L.J. Gao, J. Power Sources, 223 (2013) 306–311.
- [44] S. Suzuki, M. Miyayama, J. Power Sources. 196 (2011) 2269–2273.

Figure Captions

Fig. 1. FESEM images of electrospun nanofibers (left) and carbon nanofibers treated at different HTTs (right) of PB9/1(a), PB8/2(b), and PB7/3(c).

Fig. 2. HRTEM images of carbon nanofibers treated at different HTTs of PB9/1(a), PB8/2(b), and PB7/3(c).

Fig. 3. XRD patterns of different PB-CNFs.

Fig. 4. Galvanostatic charge–discharge curves of different PB-CNFs at current density of 20 mA g^{-1} for the 1st cycle.

Fig. 5. (a) Variations of the specific discharge capacities as a function of HTT in LIBs during the 1st cycle at a current density of 20 mA g^{-1} . (b) CV curves of the PB7/3-800 anode between 0 and 2.5 V at a scan rate of 0.1 mV s^{-1} .

Fig. 6. Rate performances (a) and cycling performances at a current density of 0.1 A g^{-1} (b) of the samples prepared at different HTTs with the 7/3 ratio of PAN to RB.

Fig. 7. (a₁, a₂) Digital images of PB7/3-1300 electrode before and after cycles. (b) SEM images of the PB7/3-1300 electrode after 100 charge–discharge cycles.

Table 1 Electrospinning formulae and HTTs of PB-CNFs.

Sample	Electrospinning formulae			HTTs (°C)
	PAN (g)	RB (g)	DMF (g)	
PB9/1-800	0.72	0.08	5.28	800
PB9/1-1000	0.72	0.08	5.28	1000
PB9/1-1300	0.72	0.08	5.28	1300
PB8/2-800	0.72	0.18	5.28	800
PB8/2-1000	0.72	0.18	5.28	1000
PB8/2-1300	0.72	0.18	5.28	1300
PB7/3-800	0.72	0.31	5.28	800
PB7/3-1000	0.72	0.31	5.28	1000
PB7/3-1300	0.72	0.31	5.28	1300

Table 2 Physical Parameters and Electrochemical Properties for different PB-CNFs.

Sample	d_{002} (Å)	Lc (nm)	S_{BET}^a ($m^2 g^{-1}$)	Q_C^b (mAh g^{-1})	Q_D^c (mAh g^{-1})	CE ^d (%)
PB9/1-800	4.26	0.97	15.36	580.3	981.9	59.1
PB9/1-1000	4.20	1.09	26.76	537.6	847.7	63.4
PB9/1-1300	4.15	1.25	31.28	250.3	380.4	65.8
PB8/2-800	4.36	0.89	14.14	598.7	956.4	62.6
PB8/2-1000	4.31	1.03	25.92	550.3	849.2	64.8
PB8/2-1300	4.28	1.15	29.25	267.6	395.9	67.6
PB7/3-800	4.45	0.79	11.43	613.4	937.9	65.4
PB7/3-1000	4.40	0.92	22.38	566.5	841.8	67.3
PB7/3-1300	4.33	1.04	27.57	286.1	408.1	70.1

^a BET surface area.
^b The charge capacity in the first cycle.
^c The discharge capacity in the first cycle.
^d The initial coulombic efficiency.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7