

Supporting Information

Lignin-derived Fused Electrospun Carbon Fibrous Mats as High Performance Anode Materials for Lithium Ion Batteries

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Preparation of the N-doped carbon fibers

For the preparation of N-doped carbon fibers, we have tried to immerse the as-spun fibers as well as the stabilized fibers (the mechanical strength of which are very weak) in urea aqueous solution first and then carry out carbonization directly at 900 °C for 2 h. However, the resulting carbon fibrous mats were very brittle and can easily break when being punched. **Figure S1** shows the morphology of the resulting carbon fibers with large quantities of macropores and cracks within the fibers, accounting for their poor mechanical strength.

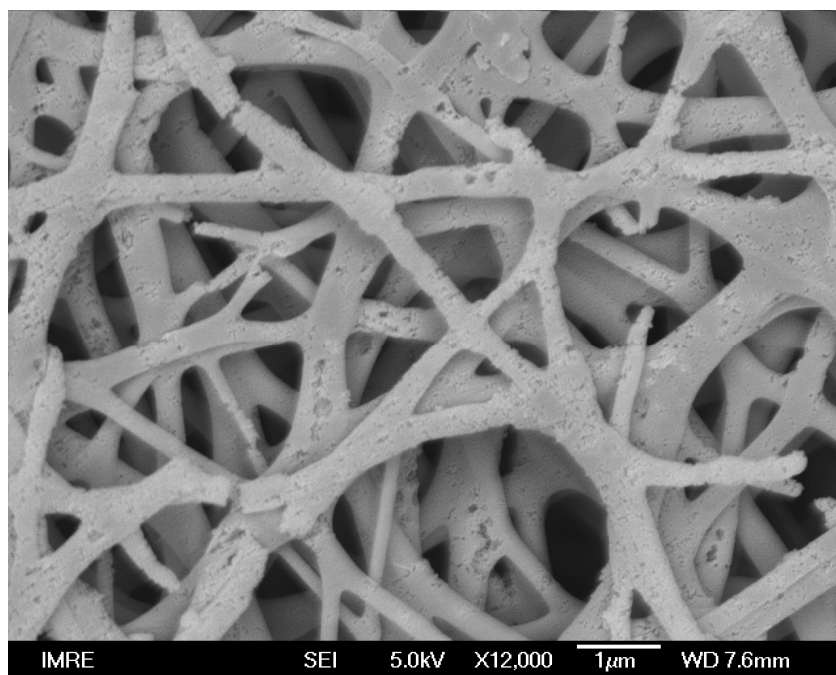


Figure S1. SEM image of N-doped carbon fibers with poor mechanical strength.

In order to obtain N-doped carbon fibrous mats tough enough to be punched to free-standing electrode materials, we first did carbonization at a low temperature (500 °C) to preform “soft” carbon fiber mats with good mechanical strength, which were subsequently immersed in urea aqueous solution and subjected to a second carbonization at 900 °C to realize nitrogen doping and higher degree of graphitization. The resulting N-doped carbon fibrous mats were tough enough to be punched and a high content of nitrogen (12.6 wt% according to elemental analysis) was doped very uniformly within the fibers (as revealed by the EDS mapping images in **Figure 2**).

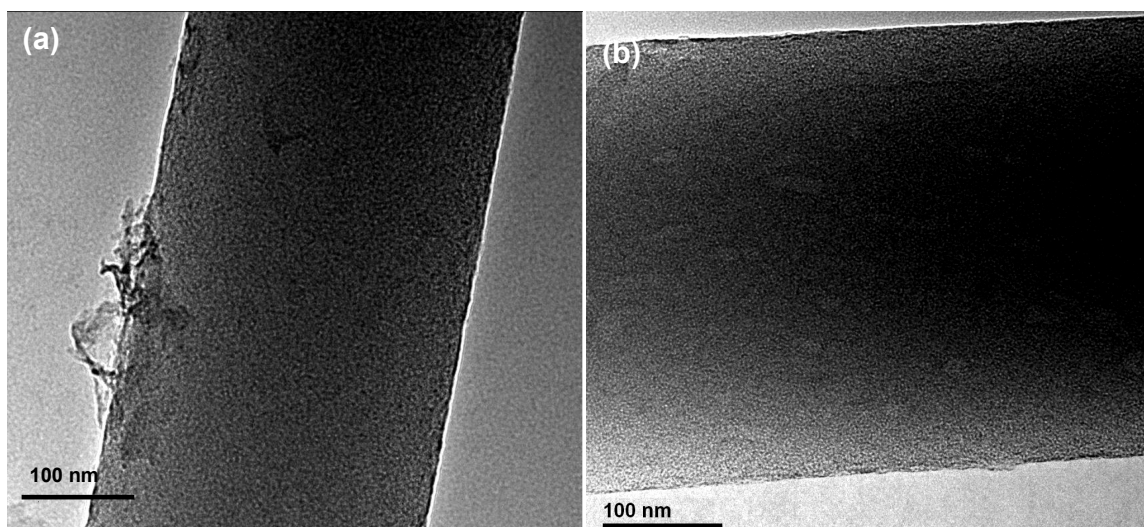


Figure S2. High resolution TEM images of the carbon fibers (a) before and (b) after nitrogen-doping.

Fused carbon fibers from lignin with two stages of carbonization (500 °C & 900 °C)

To better demonstrate the effects of nitrogen doping, we fabricated fused carbon fibers without nitrogen doping through two stages of carbonization (500 °C for 2 h followed by 900 °C for 2 h). The heat treatment condition is the same as that of the N-doped ones. Compared to the fused carbon fibers prepared via direct carbonization at 900 °C, the ones with extra heat treatment at 500 °C possess similar average pore size and pore volume, but a bit lower BET surface area of 441 m²/g (as shown in **Table S1**). However, this does not have obvious effect on their electrochemical performance. As shown in **Figure S3**, the initial charge capacity of the fused carbon fibers via two stages of carbonization could reach 452 mAh g⁻¹, and the capacitance can still maintain 425 mAh g⁻¹ at the 10th cycle. These results are quite similar with those of the fused carbon fibers directly carbonized at 900 °C (as shown in Figure 5).

Table S1. Porous structure parameters for lignin-derived carbon fibers

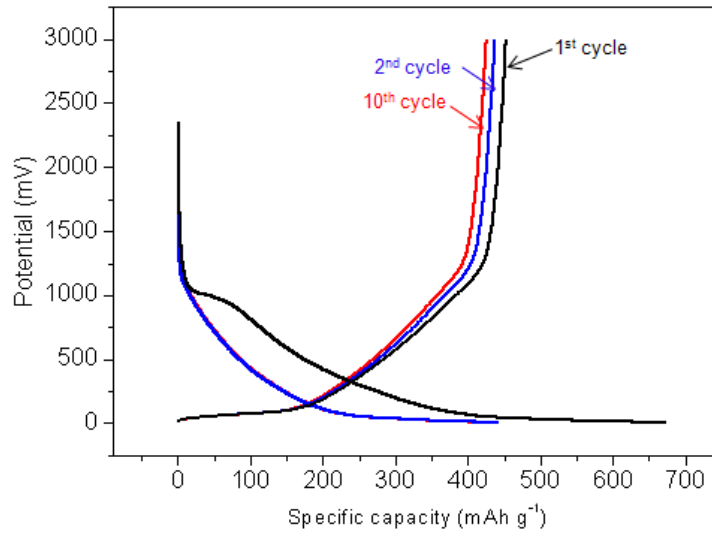
Sample name	$S_{\text{BET}}(\text{m}^2 \text{g}^{-1})^{\text{a}}$	$V_{\text{t}}(\text{cm}^3 \text{g}^{-1})^{\text{b}}$	$V_{\text{m}}(\text{cm}^3 \text{g}^{-1})^{\text{c}}$	$\text{APW}(\text{nm})^{\text{d}}$
Fused carbon fibers 1 (900 °C)	473	0.31	0.27	2.6
Fused carbon fibers 2 (500 & 900 °C)	441	0.30	0.24	2.3
N-doped fused carbon fibers	381	0.28	0.16	5.9

^a S_{BET} : BET surface area.

^b V_{t} : total pore volume measured at $P/P_0 = 0.99$.

^c V_{m} : pore volume of micropore (pore size < 2nm).

^d APW: adsorption average pore width (4V/A by BET).

**Figure S3.** Charge-discharge curves of fused carbon fibers fabricated via two stages of carbonization.

Microstructure of N-doped carbon fibers after cycling test

The morphology of the N-doped carbon fibers after 50 cycles at the charging rate of 30 mA g^{-1} is shown in **Figure S4**. The cells were cut open in a glove box filled with pure argon and the anode material was carefully taken out, washed with dimethyl carbonate (DMC) and dried under vacuum. After the cycling test, the fibrous geometry is totally intact although the surface becomes rough, which results from the repeated lithium insertion/extraction and formation of solid electrolyte interface (SEI), leading to capacity fading. After washing with 1N HCl, the lithium salts (white color substances) precipitated on the surface were completely removed, and we could observe the small cracks on the

surface of the carbon fibers (**Figure S5**). The morphology is well maintained after the cycling test, indicating the good electrochemical stability of the material.

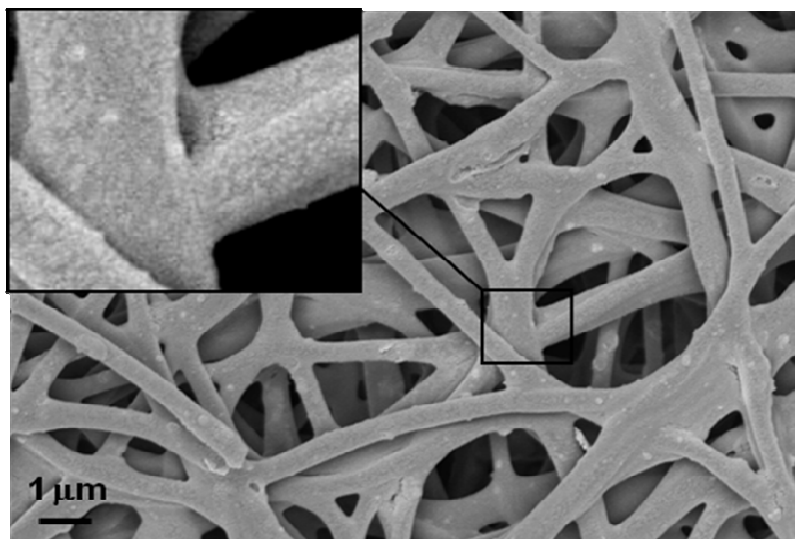


Figure S4. SEM image of N-doped carbon fibers after cycling test (before washing with HCl).

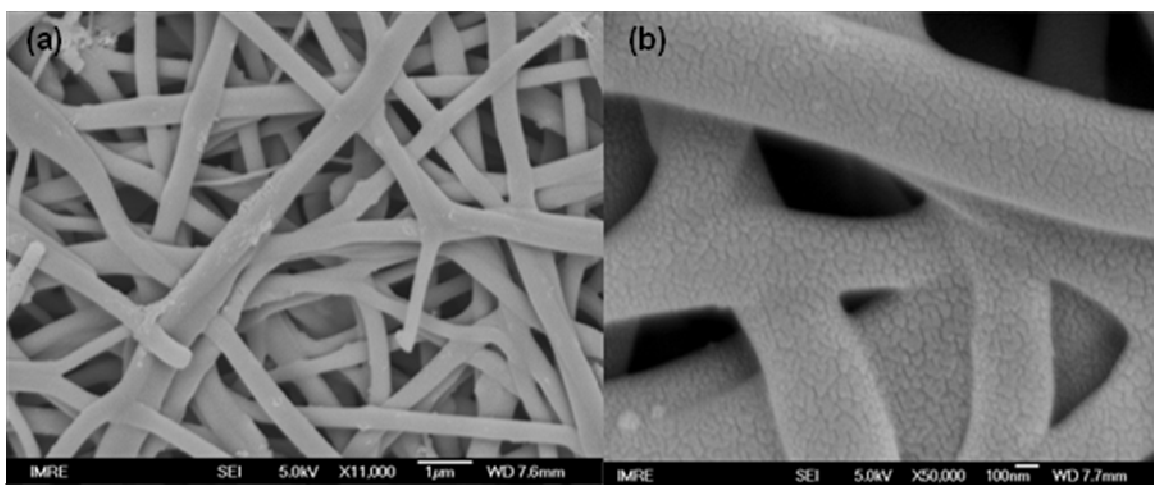


Figure S5. SEM images of N-doped carbon fibers after cycling test (after washing with HCl).