

Electrospun lignin fibers and their application

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Introduction

Lignin has attracted much attention as an alternative raw material to fossil resources. Recently, lignin-based carbon fibers are being focused on as one of value-added functional materials. So far they have been prepared by melt spinning or dry spinning followed by thermostabilization and carbonization. In this study, we attempted electrospinning and melt-electrospinning of different lignin preparations, such as acetic acid lignin (AL), soda lignin (SL) and poly(ethylene glycol)-lignin (PEGL) [1, 2], to prepare thin fibers as precursory fibers for carbon fibers (CFs) and activated carbon fibers (ACFs). Herein, we demonstrate preparation routes for CFs and ACFs, especially using modified method of thermostabilization in order to shorten its treatment time. In addition, we would like to report a new utilization of lignin-based CFs and ACFs as electrodes for electrical double layer capacitor (EDLC).

Experimental

Preparation of AL fibers by dry-electrospinning

Hardwood acetic acid lignin (HAL) was dissolved in acetic acid (AcOH) or AcOH/CCl₄ (weight ratio, 8:2), and then hexamethylenetetramine (hexamine) with different amounts was added to the solution. The mixture solution was subjected to electrospinning of lignin fibers by using a homemade electrospinning machine, and it was carried out under the following conditions: applied voltage, 38 kV; solution flow rate, 5 ml/min; tip-collector distance, 13 cm.

Preparation of SL fibers by dry-electrospinning

A mixture of softwood soda lignin (SSL) and poly(ethylene glycol) (PEG, Mw= 500 kDa) was dissolved in N,N-dimethylformamide (DMF), DMF/acetone and DMF/ethanol, and followed by heating at 80 °C for 2.5 h. The as-prepared lignin solutions were then directly electrospun under these conditions: applied voltage, 25 kV; solution flow rate, 0.5 ml/h; tip-collector distance, 13 cm.

Preparation of PEGL fibers by melt-electrospinning

PEGL alone derived from softwood or its mixture with different solvents, such as acetone, ethanol, and DMF, in different weight ratio, was melt-electrospun by a homemade spinning machine under the following conditions: Nozzle temperature, 145-150 °C; applied voltage, 20 kV; winding rate, 50 m/min.

EDLC assembly and characterization

An EDLC assembly process is shown in Fig. 1. As a first process, the electrospun lignin fibers as mentioned above were converted to CFs and ACFs. The lignin fibers were thermostabilized under air atmosphere by heating up to 250 °C at different heating rates. Then, the thermostabilized fibers were, in turn, carbonized under a nitrogen

stream at 1000 °C to yield lignin based CFs. Finally, the resultant CFs were steam activated at 900 °C. Thus, lignin based ACFs were obtained.

In the case of melt-electrospun fibers, the lignin fibers were first immersed in 6 M HCl aqueous solution at 100 °C to give chemically stabilized fibers. These fibers were further subjected to thermostabilization, carbonization and activation by the same processes as other electrospun fibers.

The resultant CFs and ACFs were grounded to powder, and suspended in aqueous carboxymethyl cellulose (CMC) solution. These suspensions were ultrasonicated to give homogeneous slurry. Then, 5% of conductive carbon black (CB) was added to the carbonaceous sample/CMC suspensions, and the mixtures were spread on an Al foil to yield electrode. The electrodes and a piece of paper sheet (Mitsubishi paper Mills Ltd. Tokyo, Japan) as a separator were immersed in triethylmethylammonium tetrafluoroborate (TEAMB₄)/propylene carbonate (PC) solution. An Al foil was placed at the bottom of electrode flat cell, and the cellulosic separator was put on the foil. Afterwards, the other Al foil was placed on the separator to give EDLC.

The performance of our EDLC was evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) method using an electrochemical workstation (Autolab PGSTAT302N FRA32M, Metrohm Autolab B.V., Japan).

Results and discussion

Preparation of lignin based fibers

The structure of lignins varies depending on the plant source and the method of isolation. Furthermore, they also affect lignin fusibility and solubility in different solvents. Herein, both dry-electrospinning and melt-electrospinning of different lignin preparations were attempted to obtain lignin fibers. Dry-electrospinning is a very simple method, which enables spinning by electrical force, and applied to most of polymer solutions to produce fine fibers, while melt-electrospinning can be applied only to polymer melt. The latter spinning costs rather low because of no use of

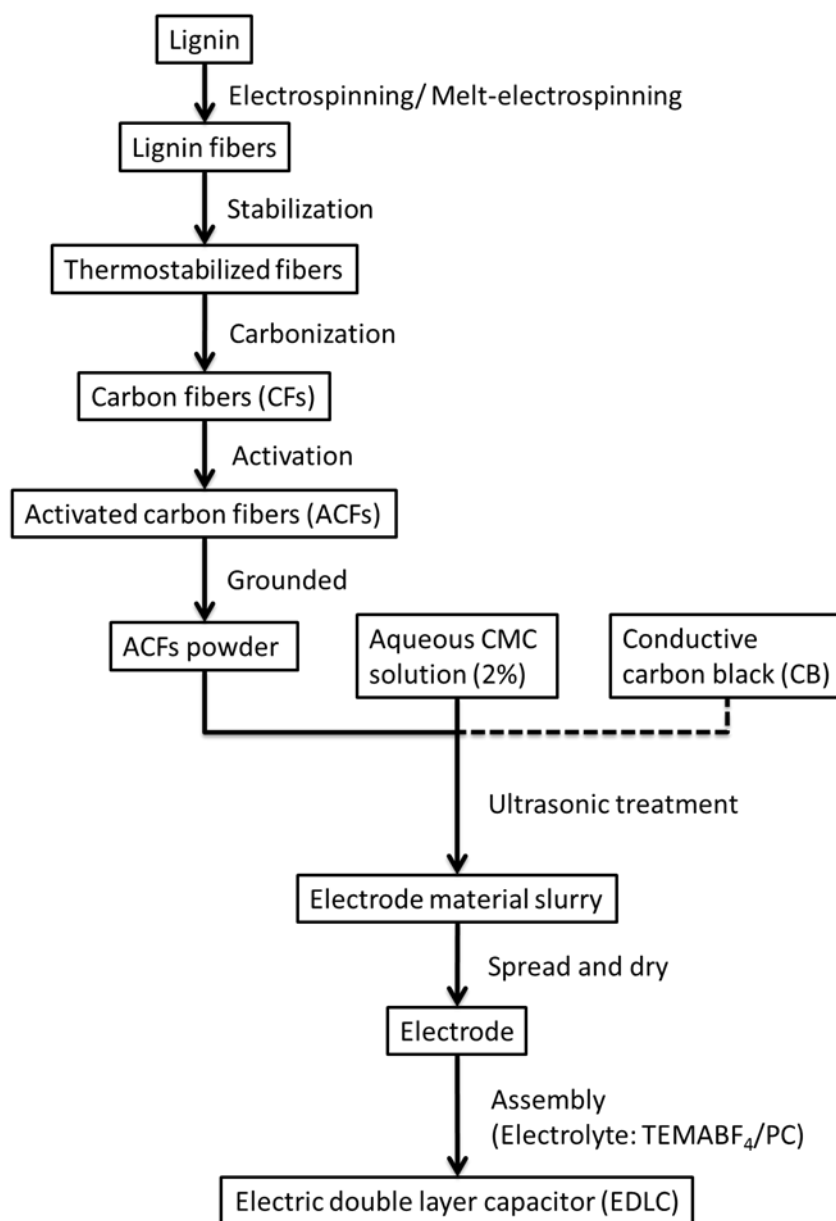


Fig. 1 A scheme for lignin-based ACF preparation and EDLC assembly

solvent. So the requirements of two methods are basically different. AL electrospun fibers (Fig. 2-A) could be obtained by dry-electrospinning from 35 wt% of AL/AcOH solution. An average fiber diameter was 1.30 μm . SL electrospun fibers (Fig. 2-B) were also prepared by dry-electrospinning from 1 wt% of PEG. On the other hand, PEGL fibers was able to be obtained by melt melt-electrospinning. However, the fiber diameter (18.0 μm) was relatively large. The diameter could be decreased by mixing PEGL with 30 wt% of DMF (Fig. 2-C). Therefore, we provided relatively feasible routes for preparing lignin-based thin fibers.

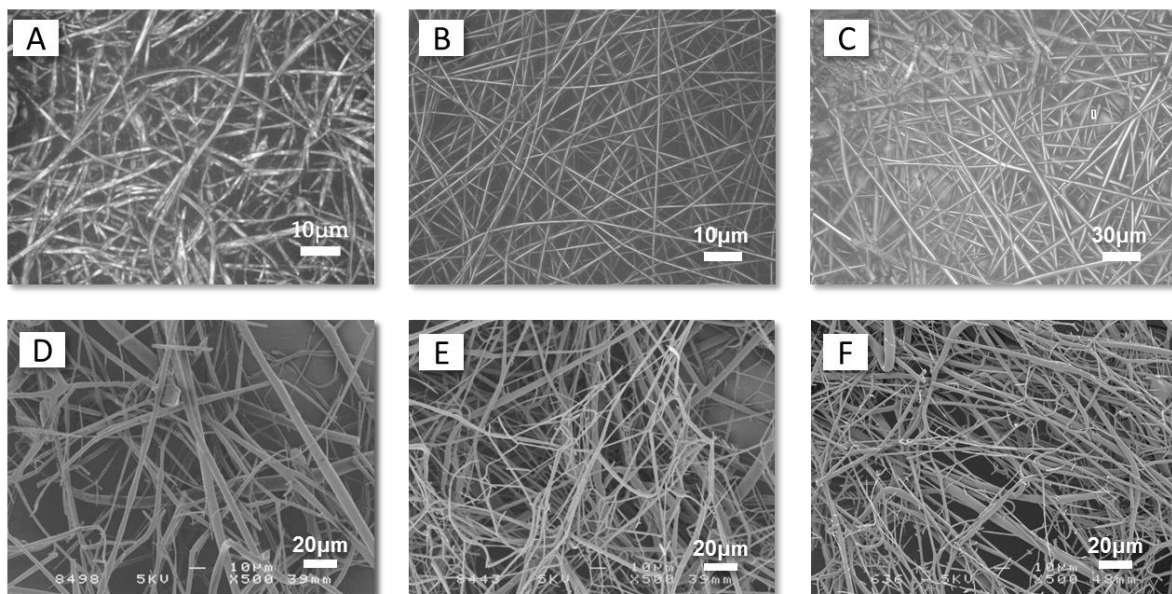


Fig. 2 Images of A) AL electrospun fibers, B) SL electrospun fibers, C) PEGL melt-electrospun fibers, and D) thermostabilized fibers, E) CFs and F) ACFs derived from AL electrospun fibers.

EDLC assembly and electrochemical characterization

The obtained fibers were converted into CFs and ACFs as a raw material for electrode of EDLC by stabilization, carbonization and activation (Fig. 1). In conventional thermostabilization process, it is carried out at 250 $^{\circ}\text{C}$ in air atmosphere for sufficient time to render them infusible by introducing oxygen molecules into lignin molecules. In general, a low heating rate is impractical because very long periods are required (i.e. for 2 days), while a high heating rate causes violent exothermic reactions resulting in a melt. Therefore, optimum stabilization conditions (heating rate, heating time and heating temperature) should be established. Thus, thermostabilization is very critical in the ACFs production process. To overcome this subject, we tried to add hexamine to the lignin solution, which was expected to act as a crosslinker to suppress thermal mobility of lignin. When hexamine was added to AL/AcOH solution, no electrospun fiber was obtained because of rapid curing before spinning. Therefore, when the reagent was applied to a mixture solvent of AcOH and CCl_4 , the dry-electrospinning of AL mixture was carried out. When the resultant fibers with 10% hexamine (on solution) were subjected to thermostabilization under air atmosphere, the infusible fibers (Fig. 2-D) were obtained by 3 h treatment. In addition, the resultant CFs (Fig. 2-E) obtained a large BET specific surface area of 1287 m^2/g even without activation. The CFs were easily converted into ACFs with the surface area of 2185 m^2/g (Fig. 2-F) by steam activation.

EDLC was assembled with the resultant CFs or ACFs as electrode materials and cellulosic paper as a separator, which contained TEAMBF₄/PC as an organic electrolyte, where commercial activated charcoal (AC) powder was also used as a reference.

As shown in Table 1, the specific electrostatic capacitance and charge transfer impedance (R_{ct}) of ACF-based EDLC were 25.1 F/g and 37.2 Ω , respectively. These electrochemical properties were remarkably superior to those of EDLC assembled with AC powder. The excellent performance was attributed to large specific surface area of ACFs. However, these values were quite low, compared to those of EDLC previously reported[3]. By the addition of CB, EDLC performance was drastically improved; R_{ct} of ACF-CB based EDLC was decreased to 12 Ω and the capacitance was remarkably increased to 133.3 F/g, which was comparable among the reported work[4]. Therefore, lignin-based ACFs can be a promising electrode material for preparing EDLC.

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Table 1. The electrochemical properties of EDLC based on different electrode materials.

Sample	Specific capacitance ¹⁾ (F/g)	Specific capacitance ²⁾ (F/g)	Charge transfer resistance (Ω)
AC powder	-	0.1	>4000
AC powder-CB	74.8	90.9	2.4
AL-ACF-2	27.9	25.1	37.2
AL-ACF-CB-2	142.0	133.3	12.0
PEGL-CF-CB	87.5	94.3	7.0

1) Specific capacitance was obtained by cyclic voltammetry

2) Specific capacitance was obtained by galvanostatic charge and discharge method.

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