Preparation of lignin-based activated carbon fibers and their application to electrodes for electric double layer capacitor

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Lignin has attracted much attention as an alternative raw material to fossil resources. Recently, lignin-based activated carbon fibers (ACFs) have been focused on as one of value-added functional materials from biomass.

An objective of my study is to prepare electrode for electric double layer capacitor (EDLC) from lignin-based ACFs as a novel utilization of lignin. To achieve this objective, I attempted to prepare fine lignin fibers by means of electrospinning and melt-spinning of three kinds of isolated lignins. The resultant lignin fibers were finally converted into ACFs by thermostabilization, carbonization and steam activation. EDLCs were assembled with the ACFs, and their electrochemical performance, such as electrostatic capacitance, intrinsic resistance and charge transfer resistance, was evaluated as compared to that of EDLC assembled with commercially available activated charcoal (AC).

1. Preparation of lignin-based ACFs and characterizations of their morphologies.

Three kinds of isolated lignins, hardwood acetic acid lignin (HAL), softwood polyethylene glycol lignin (PEGL) and softwood soda lignin (SL), were attempted to be converted into fine fibers as precursory fibers for ACFs. HAL was dissolved in acetic acid/carbon tetrachloride (AcOH/CCl₄) together with different amounts of hexamethylenetetramine (hexamine), and the solution was subjected to electrospinning. Although thermostabilization of the resultant HAL fibers was required for 38 h without hexamine to keep fibrous morphology at an elevated temperature, the time needed was dramatically shortened to 3 h by the addition of 10% hexamine based on HAL. Similarly, PEGL fibers were also obtained by electrospinning of PEGL/AcOH/CCl₄/hexamine solution. The mixture of SL and polyethylene glycol (PEG, Mw = 500 000) in N,N-dimethyl formamide could be electrospun to yield SL fibers. Melt-spinning was also conducted to prepare PEGL fibers. Finally, all the lignin fibers were converted into ACFs by aforementioned thermal treatments.

Brunauer–Emmett–Teller (BET) specific surface area of most ACFs samples were calculated from a N₂ adsorption isotherm, and were larger than 2000 m²/g. This value was much larger than that of commercial activated charcoal (AC, 1434 m²/g), which was a conventional adsorption material. In addition, micro/mesopores largely contributed to the total surface area of the lignin-based ACFs,
while macropores were responsible for that of commercial AC.

2. Assembly of single cell type of EDLC (SC-EDLC) with lignin-based ACFs and its electrochemical performance

A SC-EDLC consists of a pair of electrodes, electrolyte and a separator that is placed between the two electrodes. The electrode was prepared from a mixture of lignin-based ACFs, conductive carbon black and carboxymethyl cellulose as a binder. Two kinds of electrolytes, triethylmethylammonium tetrafluoroborate/propylene carbonate solution (TEMABF<sub>4</sub>/PC) and KOH aqueous solution, were employed as organic and aqueous electrolytes, respectively. Electrostatic capacitance of SC-EDLC was measured by cyclic voltammetry (CV) and galvanostatic charge and discharge (GCD) method, and the charge transfer resistance was determined by electrochemical impedance spectroscopy (EIS). In the organic electrolyte system, the SC-EDLC derived from electrospun HAL fibers showed the highest specific capacitance of 133.3 F/g at the current density of 1 A/g, whose value was twice that of SC-EDLC from commercial AC powder (65.2 F/g). In addition, the SC-EDLC with aqueous electrolyte exhibited 121.2 F/g, when ACFs from electrospun PEGL fibers were used. However, the value was slightly lower than that from commercial AC powder (140.2 F/g).

3. Improvement of electrochemical performance by internal tandem (IT) type lamination of electrodes

To fabricate EDLCs with a wide potential window and a high energy density, IT-EDLC was assembled by direct lamination of two and/or more pairs of electrodes with ACFs derived from melt-spun PEGL fibers in manners of series connection, parallel connection and combination connection of series/parallel (S/P comb.). As expected, the potential window was expanded by the series connection, and the total electrostatic capacitance was increased by the parallel connection according to the electrochemical theory. As a result, the energy density based on an EDLC package in the parallel-connected EDLC was remarkably increased by 66% (16.6 Wh kg<sup>-1</sup>) as compared with that of a single EDLC with a pair of electrodes. The S/P comb. connected-EDLC demonstrated both advantages.

In conclusion, lignin fibers were successfully prepared from HAL, PEGL and SL by using electrospinning and melt spinning, and these lignin fibers were converted to ACFs through a short time thermostabilization, which resulted in energy and cost savings. In addition, the resultant lignin-based ACFs had BET surface areas larger than 2000 m<sup>2</sup>/g with different pore size distributions.

SC-EDLCs were successfully prepared with all lignin-based ACFs as an electrode constituent. In organic electrolyte system, the SC-EDLC assembled with HAL-based ACFs showed the largest specific capacitance of 133.3 F/g among SC-EDLCs assembled in this study. In addition, the potential window and/or energy density of the EDLCs based on the weight of an EDLC package was remarkably improved by the internal tandem lamination of EDLC electrodes.