学位論文内容の要旨

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学位論文題名

Conversion of isolated lignins to electrode and separator of electric double layer capacitor suitable for ionic liquid electrolyte

（イオン液体電解質に適した電気二重層キャパシタ用電極およびセパレータへの単離リグニンの変換）

Nowadays, electricity storage devices are very important for creating a sustainable society on the usage of renewable energy. An electric double layer capacitor (EDLC) with high power density, long cycle life, and short charging time is focused on as a complementary device to secondary batteries such as lithium-ion batteries. Taking the concept of carbon-neutral into consideration, organic parts of EDLC, *e.g.*, electrodes and separators, should be produced from renewable raw materials. Among them, lignins derived from wood are considered as a promising feedstock because they are now utilized in the limited area of industry despite their vast abundance. Therefore, this study aims to produce the organic parts of EDLC from technical lignins isolated from wood in an industrial scale.

Although EDLC has a high power density, its energy density (E) is much lower than that of the secondary battery. Thereby, EDLC with high energy density is required. As E is expressed as $E \propto CV^2$, where C is a specific capacitance and V is an applied voltage window, V strongly affects E and depends on sorts of electrolytes. Organic electrolytes and ionic liquid (IL) electrolytes are promising because they can use under wider V of 0–3 V and 0–3.5 V, respectively, than that (0–1 V) of aqueous electrolyte. You et al., (2015) reported EDLC with excellent power density (91 kW kg^{-1}) and energy density (42 Wh kg^{-1}) assembled with activated carbon fiber (ACF) prepared from acetic acid lignin (AL) and organic electrolyte. However, I considered the ACF was more suitable for IL electrolyte because the pore size in ACF was fitted to that of IL molecules rather than to that of organic electrolyte. As the first attempt of this study, I assemble EDLC with the AL-based ACF and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) as the IL electrolyte and evaluated the electrochemical performance, energy density in particular.

Hardwood kraft lignin (HKL) is easily obtained all over the world compared to AL. As a second attempt, HKL-based ACFs were prepared as electrode material for EDLC with high E, and a separator for the EDLC was also attempted. Finally, HKL-based EDLCs were assembled and characterized.

Preparation of ACF from AL and EDLC assembly

ACF was prepared by electrospinning of AL solution with 10 wt.% hexamethylenetetramine (HEX) in $AcOH/CCl_4$ (8:2 w/w) at a concentration of 35 wt.% followed by thermostabilization, carbonization, and activation with steam (64 g). A nitrogen adsorption/desorption analysis revealed that Brunauer–Emmett–Teller (BET) specific surface areas of AL-based ACF was 1700 m^2 g^{-1}. Its average pore diameter was 0.99 nm in the micropore region. From the measurement of galvanostatic charge/discharge method (GCD), the specific capacitance of EDLC assembled with AL-based ACF, IL electrolyte, and conductive carbon black (CCB) was 124.2 F g^{-1}, and the energy density was 53 Wh kg^{-1}, which were higher than those of EDLC with AL-based ACF and organic electrolyte. Thus, AL-based ACF was proved to be more suitable for EDLC with the IL electrolyte.

Preparation of HKL-based ACF and EDLC assembly

Polyethylene glycol (PEG) is a well-known material to improve the spinnability of lignin. In this study, PEG with a molar mass of 500 kDa was added to HKL solution at a ratio of HKL/PEG = 95/5 as a sacrificial polymer to generate a big pore in addition to an improving agent for spinning. Furthermore, 10 wt.% HEX was also added to the HKL solution in DMF/AcOH (6:4 w/w). Such HKL dope at a concentration of 35 wt.% gave fine electrospun fibers. The fibers were converted to ACF by thermostabilization, carbonization, and activation with steam (19 g). An EDLC was assembled with the resultant ACF via the same process as the assembly of AL-based EDLC. Unfortunately, the EDLC revealed a very low power density. This problem was overcome by changing the addition process of CCB; CCB suspension in acetone was sprayed during electrospinning, and the resultant EDLC exhibited energy density (45 Wh kg^{-1}) and power density (42 kW kg^{-1}).

In this study, I developed an easier assembly process of EDLC compared to the aforementioned method that prepared electrodes from fine particles of ground ACF. In the new process, EDLC was directly assembled from HKL-based ACF with an appearance of filter paper without grinding. The resultant EDLC showed a much higher energy density (91.5 Wh kg^{-1}) and power density (76.2 kW kg^{-1}) than those of EDLC assembled from ground ACF.

Preparation of HKL-based separator and EDLC assembly with HKL-based materials

Thermostabilized and electrospun fibers with the appearance of filter paper were demonstrated to be applicable as a separator of EDLC without further modification. This suitable property of the fibers for the separator was caused by the porous structure, which enabled the transportation of IL electrolyte with high viscosity. EDLC was assembled with ground HKL-based ACF, the IL electrolyte, and this separator. From GCD analysis, its electrochemical performance was shown to be 114.3 F g^{-1} of specific capacitance, 48.6 Wh kg^{-1} of energy density, and 178.4 kW kg^{-1} of power density. Thus, I successfully demonstrated EDLC assembly with HKL-based electrode and separator.

In this study, EDLC with high energy density (> 42 Wh kg^{-1}) were successfully fabricated from AL- and HKL-based electrodes and a separator. The high energy density of the EDLC was attributed to not only the IL electrolyte with a wide voltage window but also the suitable pore size of lignin-based ACFs for IL molecules. This study will contribute to the valorization of lignin and the development of EDLC from biomass, leading to the creation of a sustainable society based on renewable energy.