



Research paper

Electrochemical performance of activated carbons prepared from rice husk in different types of non-aqueous electrolytes

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ABSTRACT

Activated carbons (ACs) prepared from rice husk (RH), an agricultural byproduct, have mesoporosity that is obtainable from leaching of the mineral component of silica. To verify the suitability of RH-derived ACs for the use of electrode materials of electrical double-layer capacitors, we evaluated the electrochemical performance of three RH-derived ACs (two micro- and mesoporous ACs and one mesoporous AC). Evaluation was done by using the non-aqueous ionic electrolyte solutions 1 mol dm⁻³ triethylmethyl ammonium tetrafluoroborate/propylene carbonate (PC) solution, 1.5 mol dm⁻³ spiro-(1,1')-bipyrrolidinium tetrafluoroborate/PC (SBP·BF₄/PC) solution, and the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm·BF₄). Under low voltage scan rate (1 mV s⁻¹) and low current density (<1 mA cm⁻²), mesoporous AC, which had the highest specific surface area, showed the highest specific capacitance (120 F g⁻¹) in EMIm·BF₄. However, its specific capacitance considerably decreased because of the increase in scan rate and current density. Under high scan rate (10 and 100 mV s⁻¹) and high current density (>10 mA cm⁻²), micro- and mesoporous AC in 1.5 mol dm⁻³ SBP·BF₄/PC showed the highest specific capacitance and highest retention of specific capacitance, even though its specific surface area was not the highest. Mesoporous AC showed voltage-dependent specific capacitance, indicating that ionic transport in the mesoporous structure was sensitive to electric field. It was finally shown that micro- and mesoporosity developed by utilizing natural structure and composition of RH was useful for the electrode materials of advanced electrical double-layer capacitors requiring more viscous non-aqueous electrolytes.

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1. Introduction

Electric double-layer capacitors (EDLCs), alternatively known as supercapacitors, effectively enable numerous charge–discharge cycles, as well as provide high power density, long life, and high efficiency. In combination with other power sources, EDLCs have potential of meeting the increasingly stringent specifications of next-generation vehicles (electric vehicles and fuel cell vehicles) [1] and of adopting renewable energy such as solar and wind power [2]. The mechanism of power storage by EDLCs is electrical polarization of the interface between the electrode material and the electrolyte, which allows stable and efficient charge–discharge cycles. Formation of a wider double-layer with more charge at the interface leads to higher capacitance of EDLC devices. Activated

carbons (ACs) are one of the suitable electrode materials for EDLCs because of their large specific surface area (approximately, 1000–3000 m² g⁻¹), low cost, high chemical stability, and high electrical conductivity. The pore structure of ACs is closely related to the capacitive and resistive behaviors of EDLCs. An abundance of micropores can increase the area of the interface between the electrode and electrolyte. However, ionic mobility in electrolyte in the micropores is insufficient [3]. Recent non-aqueous electrolytes which enable high withstanding voltage and thus high energy density further restrict utilization of micropores because of their high viscosity.

The type of electrolyte is a critical factor that determines the accessibility of ions to pores. The appropriate cation, anion, and solvent can enhance the EDLC performance [4–6]. Typical non-aqueous electrolyte systems for EDLC applications are quaternary ammonium salts dispersed in solvents of carbonates, for example, tetraethyl ammonium tetrafluoroborate/propylene carbonate (TEA·BF₄/PC) and triethylmethyl ammonium tetrafluoroborate/

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propylene carbonate (TEMA·BF₄/PC) mixtures. In such electrolytes, ionic mobility can be influenced by the solvent type, ion concentration, and pore structure of the electrode [7]. Spiro-(1,1′)-bipyridinium tetrafluoroborate/PC (SBP·BF₄/PC) solution has been used as alternative electrolyte to conventional quaternary ammonia electrolytes [8–14]. The performance of SBP·BF₄/PC was better in comparison with that obtained with conventional non-aqueous electrolytes [10,14]. Ionic liquids have been used as EDLC electrolytes because of their advantages such as nonvolatility and nonflammability [15–17]. Ionic liquids, which are liquids composed only of salt (anion and cation), may be used to improve the affinity of cations and anions to the pore surfaces to enhance the electrochemical performance [18].

Attention has been paid to the role of mesopores produced in ACs in enhancing the utilization of exposed pore surfaces. Highly mesoporous AC (95% mesopore volume fraction) has been shown to exhibit good electrochemical performance in a non-aqueous electrolyte [19]. The presence of mesopores could shorten the path length for ion transport in micropores and could alleviate pore blockage in micropores due to aggregation of ions while decreasing the interfacial area between the electrode and electrolyte.

Rice is a staple food in many countries. Annual rice production worldwide is 571 Tg, about one-fifth of which generates the agricultural byproduct rice husk (RH) [20]. The major constituents of RH are cellulose, hemicellulose, lignin, and, mineral components. Silica is a main ingredient of the mineral components. Silica is distributed in RH in a micro to nano scale, and the mass fraction of silica is ca. 20% [21]. This is a peculiar property which is hardly seen in other biomass species. Silica scarcely develops porous structure in RH char, but it can function as a template for mesopores [22]. Because of the great need for utilizing abundant RH, the preparation of RH-based mesoporous ACs has been intensively studied. This was done by a combination of the silica-leaching process and physical or chemical activation [23–27] or through chemical activation using strong alkalis such as NaOH or KOH [28–30].

Biomass-based ACs intended for EDLC applications have been extensively studied: waste coffee ground [31,32], cherry stone [33], waste paper [34], straw [35], sunflower seed shell [36], ginkgo shell [37], argan seed shell [38], potato starch [39], tannin [40], sucrose [41,42], lignin [43]. The electrochemical performance of RH-derived ACs in aqueous electrolytes, namely, 3 mol dm⁻³ KCl [44], 6 mol dm⁻³ KOH [45,46], 1 mol dm⁻³ Na₂SO₄ [47], and 0.5 mol dm⁻³ K₂SO₄ solutions [48], have been found to be comparable with other biomass-based ACs used for EDLC electrodes; their specific capacitances ranged approximately from 80 F g⁻¹ to 280 F g⁻¹. However, the use in non-aqueous electrolytes with higher viscosity and lower conductivity than those of aqueous electrolytes is capable of exerting the full potential of RH-derived ACs with designed mesoporosity. We proposed the fabrication of micro- and mesoporous ACs for EDLC applications using RH as a main ingredient. We used beet sugar to construct an additional microporous structure from which we removed silica to form a template for mesoporous structure [49]. The electrochemical performance of RH-derived ACs in conventional non-aqueous electrolyte of TEA·BF₄/PC [50] or TEMA·BF₄/PC [49] has been reported, in which they showed excellent performances. However, the electrochemical performance of RH-derived ACs in other non-aqueous electrolytes has not been reported.

It would be environmentally and industrially beneficial to convert RH agricultural waste into electrodes of advanced EDLCs using various types of non-aqueous electrolytes. In the present study, we examined the electrochemical performance of RH-derived micro- and mesoporous ACs and of a mesoporous AC in

three electrolytes, namely, conventional 1 mol dm⁻³ TEMA·BF₄/PC solution, alternative 1.5 mol dm⁻³ SBP·BF₄/PC solution and ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm·BF₄). The roles of microporosity and mesoporosity in their electrochemical performance were also discussed, which elucidated a compatibility of porosity designed in the RH-derived ACs with both conventional and other non-aqueous electrolytes. The results obtained would help to find promising materials for EDLC electrodes in various non-aqueous electrolytes and to understand the interaction between pore structure in ACs and those electrolytes.

2. Experimental

2.1. Sample ACs and their characterization

We obtained raw RHs by threshing rice (*Oryza sativa* L. subsp. *japonica*) harvested in south region of Akita Prefecture (40–39°N), Japan. The rice cultivar was Akitakomachi. The RHs were naturally dried and then stored indoors. Prior to the preparation of RH-derived ACs, they were dried at 378 K for 3 h in a dry oven. We previously reported the preparation processes of RH-derived ACs using the above raw RHs and beet sugar (BS, Hokuren Agriculture Cooperative Association, Japan) which was added to enhance the microporosity of RH-derived ACs [49]. The three ACs, RHBSAC0.5h, RHBSAC1.0h, and RHAC mentioned in [49], were used as sample ACs of EDLC electrodes. RHBSAC0.5h and RHBSAC1.0h are micro- and mesoporous ACs prepared from RH and BS through the silica leaching process using NaOH solution. The preparation processes of RHBSAC0.5h and RHBSAC1.0h are summarized as follows. The mixture of BS and distilled water was heated at 333 K, providing beet syrup. The RH pre-carbonized at 523 K in N₂ gas was mixed with beet syrup, and the mixture was carbonized in N₂ gas at 873 K. The carbonized mixture was immersed in NaOH solution at 1 mol dm⁻³ at 353 K for 10 h for the silica leaching. Then, it was washed using distilled water and dried in air at 378 K. Finally, it was subjected to activation process in CO₂ gas at 1123 K. The durations for the activation of RHBSAC0.5h and RHBSAC1.0h were 0.5 and 1.0 h, respectively. On the other hand, RHAC, which had a mesoporous structure, was prepared without using BS. The raw RH was carbonized in enclosed space at 773 K and then subjected to the silica leaching. The leaching process was similar to that of RHBSAC0.5h and RHBSAC1.0h. The resultant RH was washed, dried and subjected to steam activation at 1273 K, finally providing RHAC sample. All the sample ACs were pulverized into particles of <15 μm size.

The textural properties of the RH-derived ACs were evaluated from nitrogen adsorption–desorption isotherms obtained at 77 K and analyzed according to reported methodology and data [49] summarized in Table 1. The pore size distribution was evaluated by using quenched solid density functional theory under the carbon slit-shaped pore model. The width, *w*, of micropores was <2 nm, and *w* of mesopores was from 2 nm to 50 nm. Micropores and mesopores were classified as small or large. Micropores were distinguished as either ultramicropores (*w* ≤ 0.7 nm) or supermicropores (0.7 nm < *w* ≤ 2 nm), in accordance with Sing et al. [51]. Mesopores were distinguished as small mesopores (2 nm < *w* ≤ 5 nm) or large mesopores (5 nm < *w* ≤ 50 nm), which is based on the simulation result that mesopores *w* ≤ 5 nm were influential on the specific area capacitance of diffuse layer in use of 1 mol dm⁻³ TEMA·BF₄/PC solution [52]. There are no strict definitions of micro- and mesoporous structure. In the present study, micro- and mesoporous structure was defined to have micropore and mesopore volume fractions between 40% and 60% [49]. Thus, RHBSAC0.5h and RHBSAC1.0h belong to micro- and mesoporous

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