



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

Electric double-layer capacitance of carbon electrodes with high surface areas derived from shochu waste

Daisuke Tashima, Takuya Eguchi, Takashi Kumamoto, Masumi Fukuma, Seiji Kumagai

Abstract—Electric double-layer capacitors (EDLCs) are high speed chargeable/dischargeable devices. However, a lack of inexpensive electrode materials currently impedes the broad commercialization of this technology. In this work, we demonstrate low-cost activated carbon electrodes fabricated from used shochu waste and investigate their surface and electrochemical characteristics for the first time. The optimal times and temperatures for the activation of the KOH-CO₂ double-step reactions were determined. In addition, the obtained shochu waste carbons (SWCs) were used as the polarized electrodes of EDLCs, whose half-cell capacitances were evaluated using cyclic voltammetry, while their electrolyte and charge transfer resistances were estimated by measuring the corresponding AC impedance. The full-cell capacitances were evaluated based on their charge-discharge characteristics, while their internal resistances were measured by a voltage drop. Carbonization of shochu waste for 1 h at 600 °C followed by KOH activation for 1 h at 820 °C produced SWCs with the highest BET surface area (2656 m²/g) and adjacent micro pore distances ≤ 2 nm, which contributed to the formation of an electric double layer. The capacitors fabricated from such SWCs exhibited maximum capacitances of 326 F/g and 186 F/g in a 0.5 M H₂SO₄ aqueous electrolyte solution and a 0.8 M (C₂H₅)₄NBF₄/propylene carbonate organic electrolyte solution, respectively, which were much higher than the capacitances typically observed for commercial EDLCs in aqueous and organic electrolytes (284 F/g and 157 F/g, respectively) in a half-cell study. Hence, the prepared SWCs can be potentially used as high-quality electrode materials.

Index Terms— Double-Layer Capacitor, Polarized Carbon Electrode, Shochu Waste, Micro Porous Activated Carbon, Cyclic Voltammetry, Electrolyte.

I. INTRODUCTION

The use of electric double-layer capacitors (EDLCs) [1] as secondary energy storage devices has been considered in many countries. They have attracted significant attention because of their ability to serve as power supplies for electric vehicles/heavy machines and address the growing demand for high-power-density storage devices. EDLCs, which typically contain activated carbons as the primary constituents, have a remarkably long service life (compared to that of chemical batteries) and excellent discharge characteristics. These devices can store charge and electrostatic energy in the double layer that forms at the interface between the nanoporous electrode and the electrolyte solution.

Activated carbons are often used as the nanoporous electrode for EDLCs because they have high specific surface areas. In addition, such electrodes undergo minimal deterioration through a wide range of applied potentials, exhibit good cycling characteristics, and do not require maintenance. Therefore, electrochemical studies on carbon-based electrodes [2-10] and carbon based materials from biomass [11-13] have been conducted on a global scale.

In our recent work, we attempted to increase the electrical capacitance of EDLCs by using carbon nanospheres [14] and wires [15], and modifying the surface of carbon materials [16, 17]. As a result, the specific capacitances of these devices were enhanced; however, the proposed solutions also significantly increased their costs. Reducing the material costs and improving device performances, which represent the two main goals of our study, would make EDLCs more economically attractive. In this work, the first step in this direction was made by showing that the exceptional specific capacitance of EDLCs could be obtained using organic waste (in particular, discarded shochu (Japanese liquor) waste). The second step was to achieve a high energy density that could be sufficient for their applications in electric vehicles or power-assist machines. Many possible recycling methods for shochu waste are reported in the literature [18-21]; however, we are not aware of any publications that examine electrical storage devices fabricated from shochu waste, except for gas storage [22]. Recently, the disposal of large amounts of shochu waste has become a serious problem in the southern regions of Japan; thus, the present study



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

suggests a plausible method for reusing shochu waste to produce low-cost large-capacitance/high-energy density carbon materials for EDLCs. Shochu is made from many natural constituents, e.g., potato, wheat, buckwheat, rice, and sesame. Potato (sweet potato variety) shochu waste was used in this research. In particular, micro-mesoporous activated carbons with high surface areas were synthesized from shochu waste through the KOH-CO₂ double-step activation stages, and their application as polarized electrodes for EDLCs was evaluated by investigating their surface morphology, electrochemical capacitance, AC impedance, charge-discharge characteristics, and internal resistances.

II. EXPERIMENTAL

A. Preparation and characterization of shochu waste carbons

Shochu waste was provided by a shochu liquor company in Japan (the original waste was mostly liquid, and the remaining bulk elements were separated using a centrifuge). The extracted shochu waste was dried at 70 °C for 20 h followed by carbonization in a tube furnace (TMF-500N, As One Co., Japan) under N₂ gas flow at a temperature of 600 °C and heating rate of 5 °C/min for 1 h. The KOH activation process required soaking of the carbonized shochu waste in an 8 M KOH solution for more than 24 h; as a result, the carbonized shochu waste/KOH weight ratio was 1/2. One of the problems encountered during the fabrication procedure was the corrosion of the tube furnace caused by its interaction with the highly alkaline KOH reagent. Hence, corrosion-related maintenance costs were reduced by using relatively low amounts of KOH. After drying, the materials were activated using KOH inside the furnace under a N₂ gas flow at 820 °C for 1 h. During CO₂ activation, the materials were kept in the furnace under a CO₂ gas flow at 850 °C for 1–3 h. Four types of SWCs were prepared using the described method and varying the CO₂ activation times. The samples were named as K1Cx (where x represents the CO₂ activation time (h); x = 0–3). The prepared SWCs were further purified by washing in a 0.6 M aqueous HCl solution, rinsing with distilled water until the pH of the wastewater reached 7, and drying at 150 °C for 1 h. The morphologies of the prepared SWCs were analyzed using scanning electron microscopy (SEM; S-5500, Hitachi High-Technologies Co., Japan). After additional drying at 150 °C for over 12 h under high vacuum (10 Pa), the surface areas and pore size distributions of the synthesized SWCs were analyzed using Brunauer-Emmett-Teller (BET) [23], t-plot [24–26], and Barrett-Joyner-Halenda (BJH) [27] measurements, which were performed using an automatic specific surface area/pore size distribution measuring system (Tristar 3000, Micromeritics Instrument Corp., USA). The thermal decomposition behavior of the utilized shochu waste was investigated using thermo gravimetry/differential thermo gravimetry (TG/DTG; TG/DTA 320U, Seiko Instruments, Inc., Japan) using an open pan that was purged with N₂ gas at a heating rate of 5 °C/min, gas flow rate of 500 mL/min, and target temperature of 600 °C.

B. Half-cell cyclic voltammetry and AC impedance studies

Polarized electrodes were fabricated for the electrochemical characterization experiments. The prepared SWCs, polytetra fluoroethylene binder, and Ketjen black (EC-600JD; Lion Specialty Chemicals Co., Ltd., Japan) conducting material were mixed at a mass ratio of 8.5:0.5:1.0. The resulting mixture was poured in a mold and used to fabricate polarized electrodes with diameters of 10 mm and thicknesses of 550 μm at a pressure of 5 MPa using a heat press machine (AH-2003, AS ONE, Japan). The capacitances of the prepared electrodes were determined using an electrochemical measurement system (HZ-5000, Hokuto Denko Co. Ltd., and Japan). To characterize the organic electrolyte medium, a 0.8 M electrolyte solution was prepared by dissolving a proper amount of tetraethyl ammonium tetrafluoroborate ((C₂H₅)₄NBF₄) in propylene carbonate (PC) obtained from Tomiyama Pure Chemical Industries Ltd., Japan. A Pt counter electrode with an area of 200 mm² and an Ag/Ag⁺ reference electrode were used for cyclic voltammetry (CV) measurements conducted at sweep rates of 1 mV/s in a voltage range of 2.5 V. To evaluate the properties of the aqueous electrolyte, a 0.5 M H₂SO₄ electrolyte solution was obtained from Wako Pure Chemical Industries Ltd. (Japan). The corresponding CV measurements were performed at sweep rates of 1 mV/s in a voltage range of 1 V using the same Pt counter electrode and Ag/AgCl reference electrode. The electrolyte temperature was maintained at 20 °C using a low-temperature incubator (CSB-900N Series-2; Asone Co, Ltd., Japan). The capacitances of the produced SWCs were calculated from the results of the CV measurements. We assume that when the potential (*V*) applied to the working electrode is swept anodically or cathodically from *V*₁ to *V*₂ at a constant scan rate (*r*_s), the flowing current, *i*, yields the total charge of $-Q$ or $+Q$ after time, *t*, during each scan. The total charge magnitude was estimated as one-half of the area, *S*_c, under the rectangular *i*-*V* curve, which was subsequently divided by the mass of the activated carbon materials, *m* (g). Hence, the capacitance, *C* (F/g), of the obtained EDLC was evaluated from the total one-way scan time, *t*_s (s),



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 6, Issue 6, November 2017

using the following formula:

$$C = \int_0^{t_s} i dt / m \int_{V_1}^{V_2} dV = \frac{1}{r_s} \int_{V_1}^{V_2} i dV / m \int_{V_1}^{V_2} dV = \frac{1}{2r_s} S_c / m (V_2 - V_1) \quad (1)$$

The complex impedance of the EDLC cells was determined by an AC two-electrode method using a FRA5020 impedance measurement system (Hokuto Denko Co. Ltd., Japan). An AC current of 0.2 mA was applied across the EDLC cells in the frequency range from 10 mHz to 20 kHz.

C. Full-cell charge and discharge studies

Using a charge/discharge testing device (CDT510-4) fabricated by Power Systems Corp. (Japan), the manufactured EDLCs were fully charged at charging current densities of 125, 250, 500, 750, and 1000 mA/g. Then, the devices were charged to saturation for an additional 15 min and then discharged at constant discharging current densities of 125, 250, 500, 750, and 1000 mA/g, respectively. As organic electrolytes, a 0.8 M $(C_2H_5)_4NBF_4$ solution in PC obtained from Tomiyama Pure Chemical Industries Ltd.(Japan) and 1.5 M 1,1-(tetramethylene)pyrrolidinium tetrafluoroborate (SBPBF₄) solution in PC obtained from Japan Carlit Co., Ltd. were used. The charging voltage at full charge was set to 2.5 V for the $(C_2H_5)_4NBF_4/PC$ system and 3.2 V for the SBPBF₄/PC system after considering the electrolyte decomposition voltage and the charge/discharge testing procedure. The specific capacitances of the EDLC cells were calculated using the following formulas:

$$U = C \times V^2 / 2 \quad (2)$$

$$C = 2 \times U / (V^2 \times m) \quad (3)$$

where U , C , V , and m are the discharge energy (J), specific capacitance (F/g), discharge voltage after voltage drop (V), and mass of the active carbon materials (g), respectively. Moreover, the EDLC internal resistance was determined from the difference between the voltage at the beginning of the discharge process and the voltage drop.

III. RESULTS AND DISCUSSION

A. Characteristics of the produced nanocarbons

Figure 1(a) shows the original dried shochu waste. The resultant surface morphologies of the carbonized sample and activated SWCs consist of porous structures (Fig. 1(b-c)). The activated SWCs contain multiple pores <10 μ m, which enabled transportation of the stored anions and cations (Fig. 1(d)). The N_2 adsorption-desorption isotherms obtained at -196 °C for the K1Cx ($x = 0-3$) SWC samples and commercially available KOH-activated carbon are shown in Fig. 2(a). The N_2 adsorption isotherms of the synthesized SWCs correspond to typical type I isotherms according to the IUPAC classification; such isotherms are usually produced by micro porous materials with small external surface areas because their limited uptake mostly depends on the accessible micro pore volume and not on the internal surface area.

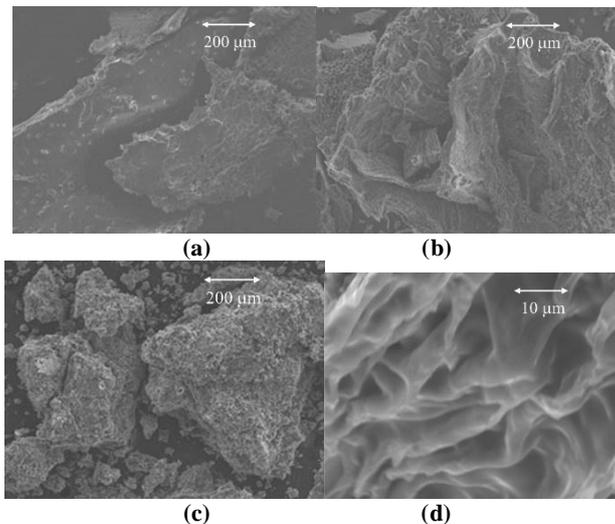


Fig 1 SEM images of the (a) shochu waste, (b) carbonized SWCs, (c) activated SWCs, and (d) activated SWCs at a higher magnification.

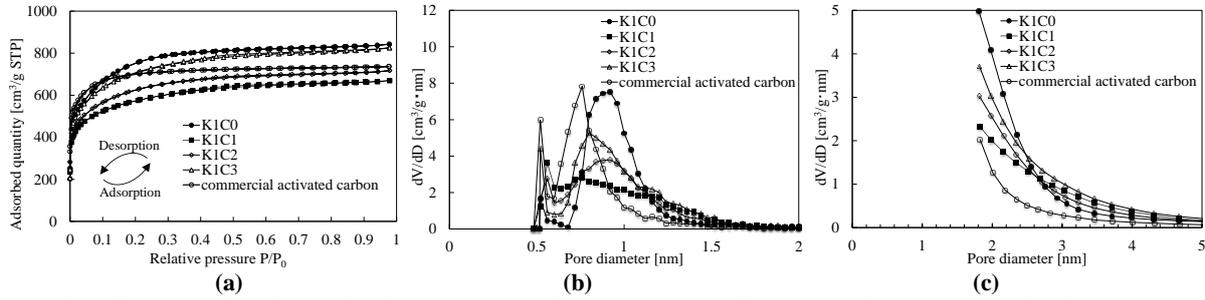
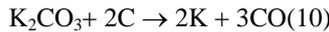
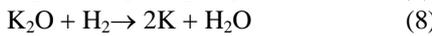


Fig 2(a) N₂ adsorption–desorption isotherms, (b) micropore size distributions, and (c) mesopore size distributions obtained for the K1Cx(x = 0–3) samples and commercially available activated carbon.

Two distinct phenomena are observed for the adsorption-desorption isotherms. The initial rapid adsorption at $P/P_0 = 0-0.3$ exhibited by each of the samples is mainly due to the N₂ adsorption in the micropores, while the subsequent gradual adsorption over a wide range of relative pressures ($0.3 < P/P_0 < 0.9$) likely occurs because of capillary condensation of N₂ inside the mesopores. In addition to the adsorption-desorption isotherms described above, the related micro pore/mesopore-diameter distribution curves were recorded (the obtained BET surface areas (S_{BET}), micro pore volumes (V_{micro}), and mesopore volumes (V_{meso}) are listed in Table 1). The K1C0 SWC sample exhibits an S_{BET} value of 2656 m²/g, which is the largest BET surface area among the studied samples. The values of S_{BET} and V_{micro} decrease after 1 h of CO₂ activation and then increase after 2–3 h of CO₂ activation. The values of V_{meso} increase with increasing CO₂ activation times. The S_{BET} value of the K1C3 sample is 2441 m²/g, which is almost the same value as that for commercial activated carbon. The samples subjected to double activation exhibit a higher volume of mesopores than those of commercial activated carbon. The reaction of carbon atoms with KOH produces micro-sized pores, while the reaction of carbon atoms with CO₂ creates meso-sized pores. The pore volumes of the synthesized SWCs depend on the activation method, reaction temperature, and time. The KOH activation reaction processes are as follows:



The first step of the reaction process (Eq. 4) occurs below 500 °C. The second step of the reaction process (Eqs. 5–7) occurs between 500 and 800 °C. The final step of the reaction process (Eqs. 8–10) occurs above 800 °C. The obtained micropore and mesopore diameter distributions of the K1Cx (x = 0–3) SWC samples are shown in Fig. 2(b–c). The K1C0 SWCs have pore diameters of 0.7–1.1 nm, while the KOH-CO₂ activated SWCs contain pores with diameters ranging between 0.5 and 1.5 nm; thus, the high mesopore volumes increase the corresponding BET surface areas. Fig. 3(a–b) shows the TG and DTG analysis results for the shochu waste. As indicated by the TG curve, the rapid reduction in the sample weight originates from thermal decomposition of the natural polymers in the shochu waste. The related DTG curves show that this thermal decomposition process occurs in three consecutive steps corresponding to the predominant decomposition of hemicelluloses, cellulose, and lignin in the temperature ranges of 200–260 °C, 240–310 °C, and 310–400 °C, respectively [28–31].

Table 1. BET surface areas and pore volumes of the prepared materials.

Sample	BET surface area [m ² /g]	Pore volume (V_{micro} : < 2 nm) [cm ³ /g]	Pore volume (V_{meso} : 2–50 nm) [cm ³ /g]
K1C0	2656	0.50	0.45
K1C1	1982	0.47	0.53
K1C2	2161	0.48	0.58
K1C3	2441	0.51	0.71
Commercial carbon sample (activated with KOH)	2342	0.84	0.28

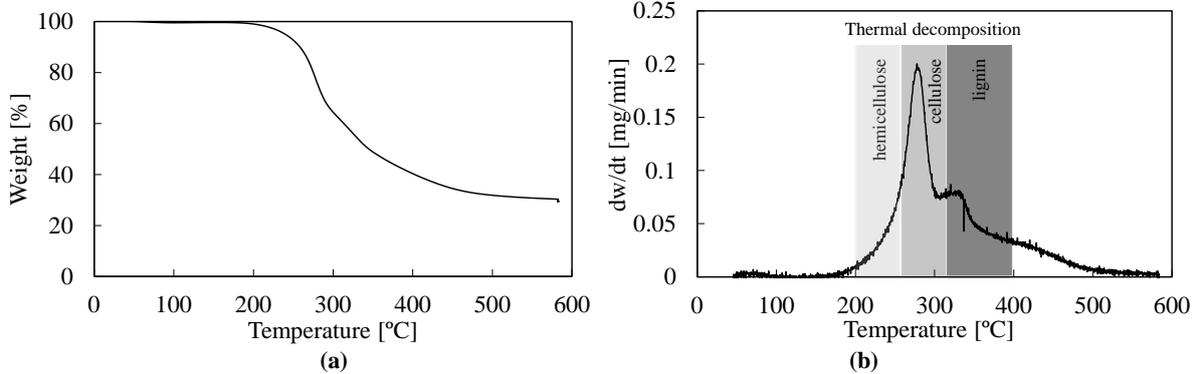


Fig 3(a) TG and (b) differential TG curves obtained for the shochu waste.

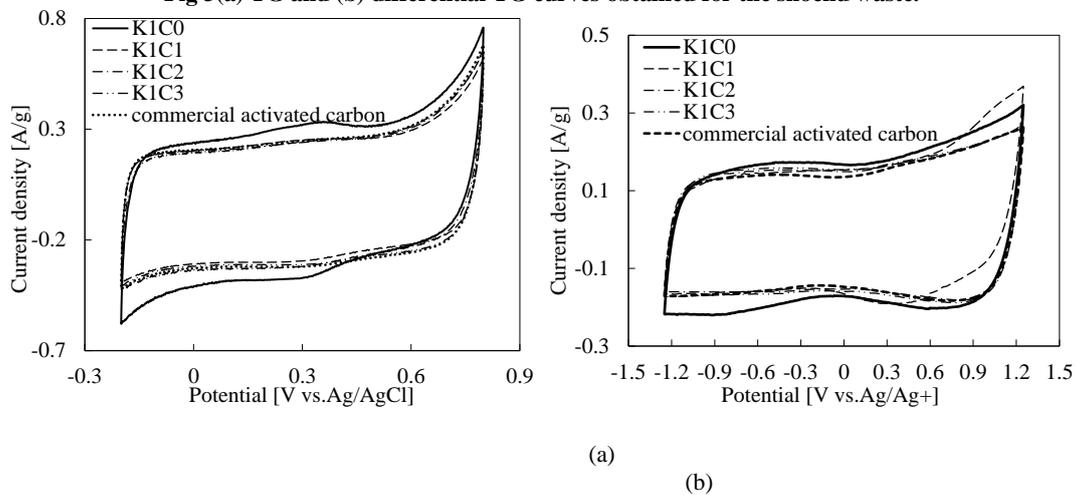


Fig 4 Cyclic voltammograms recorded in the (a) 0.5 M H₂SO₄ and (b) 0.8 M (C₂H₅)₄NBF₄/PC solutions at a sweep rate of 1 mV/s.

B. Results of the half-cell cyclic voltammetry and AC impedance studies

Fig. 4 shows the cyclic voltammograms of the polarized electrodes mixed with SWCs in (a) 0.5 M H₂SO₄ and (b) 0.8 M (C₂H₅)₄NBF₄/PC solutions, which were recorded at a sweep rate of 1 mV/s. The results indicate that the electrolytic ions first adsorb and then desorb from the surface of the working electrode with the changing voltage, while the nearly rectangular shapes of these curves suggest a predominantly capacitive response. As shown in Fig. 4(a), the measured current densities increase at both low and high applied potentials, which indicate that the surface area of the activated carbon is large and that the surface functional groups of the SWC surface likely undergo oxidation-reduction reactions. Therefore, the wettability of the electrodes is influenced by the formation of phenolic hydroxyl and carboxyl groups, while the presence of carboxyl groups causes Faradaic reactions, which increase the measured electrode capacitance (pseudo-capacitance). The use of aqueous electrolytes typically increases the capacitance of nanoporous electrodes. The highest specific capacitance of the studied samples obtained in the aqueous electrolyte is 326 F/g. In similar work using organic waste materials for EDLCs, Li et al. reported a capacitance of 268 F/g in a 6 M KOH solution using a potato-starch-based carbon nanofiber/activated carbon hybrid electrode with a surface area of 1930 m²/g [32]. Zhao et al. reported a capacitance of 335 F/g in a 6 M KOH solution using a potato-starch-based activated carbon spherical electrode with a surface area of 2342 m²/g [33]. The capacitance of 326 F/g in the 0.5 M H₂SO₄ solution was relatively higher than that for similar work using potato-starch-based materials. As shown in Fig. 4(b), the current densities measured for the K1C0 sample are higher than those of the commercially available activated carbon because of the adsorption and desorption of anions (BF₄⁻) and cations ((C₂H₅)₄N⁺). The highest specific capacitance (186 F/g) is observed for the K1C0 SWCs in the organic electrolyte (listed in Table 2) because of their large pore volume and relatively high surface area of micropores and mesopores. The double-layer capacitance of EDLCs generally depends on the surface area of the electrode, which is in turn affected by the micropore volume. The results suggest that the polarized electrode with a high micropore volume and micro-mesopore surface area can



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

adsorb a larger number of anions and cations from the organic electrolyte.

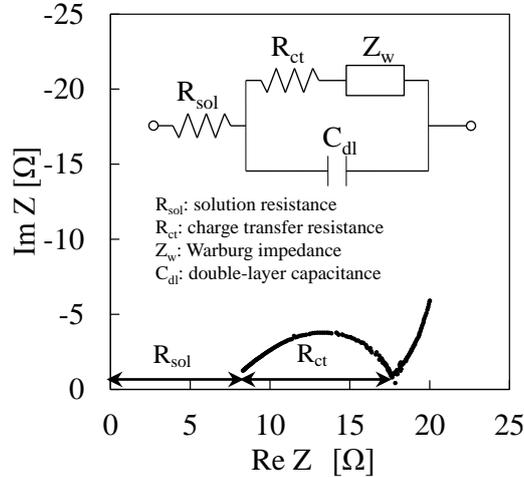


Fig 5 AC impedance spectrum of the K1C0 SWC sample recorded in a 0.8 M $(C_2H_5)_4NBF_4/PC$ solution.

Table 2. Specific capacitances and internal resistances ($R_{sol}+R_{ct}$) of the polarized electrodes mixed with SWCs obtained from half-cell cyclic voltammetry and AC impedance studies.

Sample	0.5 M H_2SO_4 electrolyte			0.8 M $(C_2H_5)_4NBF_4/PC$ electrolyte		
	Capacitance at 1 mV/s [F/g]	R_{sol} [Ω]	R_{ct} [Ω]	Capacitance at 1 mV/s [F/g]	R_{sol} [Ω]	R_{ct} [Ω]
K1C0	326	0.516	0.59	186	8.29	9.55
K1C1	266	0.542	0.52	165	8.17	10.17
K1C2	277	0.516	0.59	161	8.32	9.90
K1C3	276	0.546	0.49	166	9.50	10.23
Commercial carbon sample	284	0.466	0.59	157	6.35	9.22

The AC impedance spectrum obtained for the K1C0 SWC sample in the 0.8 M $(C_2H_5)_4NBF_4/PC$ electrolyte solution is composed of a semicircle in the frequency range of 2–20 kHz and a linear segment in the low-frequency region between 10 mHz and 2 kHz (Fig. 5). The starting point of the semicircle represents the solution resistance of the polarized electrode, and the diameter of the semicircular path indicates the charge transfer resistance. The equivalent circuit constructed for the studied EDLCs contains the charge transfer resistance (R_{ct}) and Warburg impedance (Z_w) connected in series, the double-layer capacitance (C_{dl}) connected in parallel, and the solution resistance (R_{sol}) connected in series (inset of Fig. 5). The results of the internal resistance ($R_{sol} + R_{ct}$) analysis performed using electrochemical impedance spectroscopy are listed in Table 2. They show that the KOH- CO_2 activated carbons exhibit slightly higher internal resistances than those of the commercially available activated carbons.

C. Results of the full-cell charge and discharge studies

Fig. 6(a–b) displays the charge-discharge curves recorded for a single K1C0 cell, which show current densities of 125, 250, 500, 750, and 1000 mA/g. The EDLCs in the 0.8 M $(C_2H_5)_4NBF_4/PC$ electrolyte solution were fully charged up to 2.5 V (Fig. 6(a)), while the EDLCs in the 1.5 M SBPBF₄/PC solution were fully charged up to 3.2 V (Fig. 6(b)). The observed charging and discharging times decrease with increasing current densities. Fig. 7 shows the capacitances of the SWC electrodes measured during their charge-discharge testing in the 0.8 M $(C_2H_5)_4NBF_4/PC$ and 1.5 M SBPBF₄/PC electrolyte solutions as functions of the current density (it also displays the corresponding average internal resistance, $r_{average}$). The results indicate that the capacitance of the K1C0 SWC electrode with a current density of 1000 mA/g decreases by 20.0% compared to the magnitude measured for the



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

same material with a current density of 125 mA/g in the 0.8 M $(C_2H_5)_4NBF_4/PC$ electrolyte solution. In contrast, the capacitance of the K1C0 SWC electrode with a current density of 1000 mA/g decreases by only 9.6% compared to that of the same material with a current density of 125 mA/g in the 1.5 M SBPBF₄/PC solution, indicating that the SBPBF₄/PC system maintains its specific capacitance while increasing the current density (unlike the specific capacitances in 0.8 M $(C_2H_5)_4NBF_4/PC$). Moreover, the average internal resistances of the electrodes measured in the 1.5 M SBPBF₄/PC electrolyte solution are relatively lower than that of the commercial activated carbon. Table 3 shows specific capacitances at 125 mA/g and average internal resistances of the EDLCs cell mixed with SWCs obtained from full-cell charge and discharge studies.

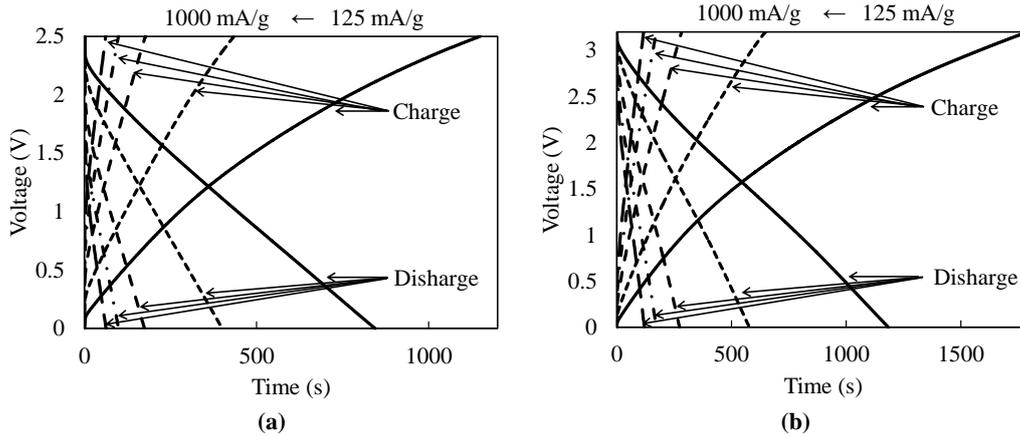


Fig 6 Charge-discharge curves obtained for a single K1C0 cell in the (A) 0.8 M $(C_2H_5)_4NBF_4/PC$ and (B) 1.5 M SBPBF₄/PC electrolyte solutions.

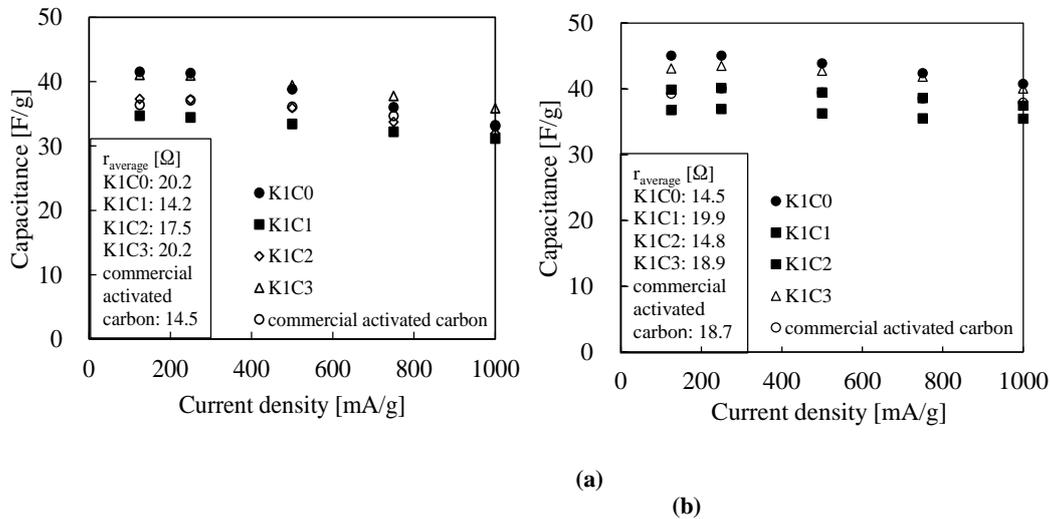


Figure 7 Charge-discharge rate characteristics of the fabricated SWC samples and commercially available activated carbon obtained in the (a) 0.8 M $(C_2H_5)_4NBF_4/PC$ and (b) 1.5 M SBPBF₄/PC electrolyte solutions.

Table 3. Specific capacitances and internal resistances of the EDLCs cell mixed with SWCs obtained from full-cell charge and discharge studies.

Sample	0.8 M $(C_2H_5)_4NBF_4/PC$ electrolyte		1.5 M SBPBF ₄ /PC electrolyte	
	Capacitance at 125 mA/g [F/g]	$R_{average}$ [Ω]	Capacitance at 125 mA/g [F/g]	$R_{average}$ [Ω]
K1C0	41.5	20.2	45.0	14.5



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

K1C1	34.7	14.2	36.8	19.9
K1C2	37.3	17.5	39.9	14.8
K1C3	41.1	20.2	43.1	18.9
Commercial carbon sample	36.4	14.5	39.3	18.7

The energy densities of the EDLCs containing the K1C0 SWC electrodes are calculated using the following formula:

$$W = U / (3600 \times m) \quad (11)$$

Where W , U , and m are the energy density (Wh/kg), discharge energy (J), and mass of a single cell (kg), respectively. The calculated energy densities are equal to 33 Wh/kg in the 0.8 M $(C_2H_5)_4NBF_4/PC$ solution at a current density of 125 mA/g and 61 Wh/kg in the 1.5 M SBPBF₄/PC solution at a current density of 125 mA/g (these values are 10–15% higher than the values obtained for the commercially available carbon). In addition, the estimated manufacturing costs of the produced SWCs decrease by a factor of about 1/3 (including the material costs and transportation fee). Therefore, the prepared SWCs can be potentially used for manufacturing low-cost EDLCs with high energy-storage capacities.

IV. CONCLUSION

In this study, activated carbon materials derived from shochu waste were utilized to fabricate nanoporous electrodes for EDLC applications, and their surface morphologies, electrochemical capacitances, AC impedances, charge-discharge characteristics, and internal resistances were examined. The obtained KOH-activated SWCs exhibited very high surface areas and large micro pore volumes, and the obtained KOH-CO₂ activated SWCs exhibited relatively high surface areas and large mesopore volumes, which contributed to the capacitances of 326 F/g and 186 F/g observed in the 0.5 M H₂SO₄ aqueous electrolyte and 0.8 M $(C_2H_5)_4NBF_4/PC$ organic electrolyte, respectively. The energy densities of single EDLC cells measured in the 0.8 M $(C_2H_5)_4NBF_4/PC$ and 1.5 M SBPBF₄/PC electrolyte solutions were 33 and 61 Wh/kg, respectively. Thus, the SWCs materials derived from shochu waste were shown to be a highly valuable source of low-cost activated carbons for manufacturing EDLC electrodes.

ACKNOWLEDGMENT

The authors thank Yoshihiro Hamasuna and Nobuhito Kamikuri, graduate students from the Department of Electrical and Electronic Engineering at the Graduate School of Engineering of the University of Miyazaki, for their help with conducting this study. Funding: This work was supported by a scientific research grant awarded by the Japan Society for the Promotion of Science KAKENHI [grant number 26420240].

REFERENCES

- [1] B. E. Conway, *Electrochemical supercapacitors : scientific fundamentals and technological applications*. New York: Plenum Press, 1999.
- [2] Q.-Y. Li, H.-Q. Wang, Q.-F. Dai, J.-H. Yang, and Y.-L. Zhong, "Novel activated carbons as electrode materials for electrochemical capacitors from a series of starch," *Solid State Ionics*, vol. 179, pp. 269-273, 2008.
- [3] M. Härmas, T. Thomberg, H. Kurig, T. Romann, A. Jänes, and E. Lust, "Microporous–mesoporous carbons for energy storage synthesized by activation of carbonaceous material by zinc chloride, potassium hydroxide or mixture of them," *Journal of Power Sources*, vol. 326, pp. 624-634, 2016.
- [4] M. Enterría, A. G. Gonçalves, M. F. R. Pereira, J. I. Martins, and J. L. Figueiredo, "Electrochemical storage mechanisms in non-stoichiometric cerium oxide/multiwalled carbon nanotube composites," *Electrochimica Acta*, vol. 209, pp. 25-35, 2016.
- [5] M. Egashira, T. Izumi, N. Yoshimoto, and M. Morita, "Determining water content in activated carbon for double-layer capacitor electrodes," *Journal of Power Sources*, vol. 326, pp. 635-640, 2016.
- [6] Y. Cao, K. Wang, X. Wang, Z. Gu, Q. Fan, W. Gibbons, et al., "Hierarchical porous activated carbon for supercapacitor derived from corn stalk core by potassium hydroxide activation," *Electrochimica Acta*, vol. 212, pp. 839-847, 2016.
- [7] S. Zhong, C. Zhan, and D. Cao, "Zeolitic imidazolate framework-derived nitrogen-doped porous carbons as high performance supercapacitor electrode materials," *Carbon*, vol. 85, pp. 51-59, 2015.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

- [8] J.-z. Wang, L.-q. Wang, M.-m. Chen, C.-y. Wang, C. Zhang, and F. He, "Nanoporous carbons from oxidized green needle coke for use in high performance supercapacitors," *Carbon*, vol. 93, p. 1082, 2015.
- [9] P. R. Choi, E. Lee, S. H. Kwon, J. C. Jung, and M.-S. Kim, "Characterization and organic electric-double-layer-capacitor application of KOH activated coal-tar-pitch-based carbons: Effect of carbonization temperature," *Journal of Physics and Chemistry of Solids*, vol. 87, pp. 72-79, 2015.
- [10] X. He, J. Lei, Y. Geng, X. Zhang, M. Wu, and M. Zheng, "Preparation of microporous activated carbon and its electrochemical performance for electric double layer capacitor," *Journal of Physics and Chemistry of Solids*, vol. 70, pp. 738-744, 2009.
- [11] G. Amaral-Labat, A. Szcurek, V. Fierro, N. Stein, C. Boulanger, A. Pizzi, et al., "Pore structure and electrochemical performances of tannin-based carbon cryogels," *Biomass and Bioenergy*, vol. 39, pp. 274-282, 2012.
- [12] K. R. Thines, E. C. Abdullah, N. M. Mubarak, and M. Ruthiraan, "In-situ polymerization of magnetic biochar – polypyrrole composite: A novel application in supercapacitor," *Biomass and Bioenergy*, vol. 98, pp. 95-111, 2017.
- [13] A. M. Dehkhoda, E. Gyenge, and N. Ellis, "A novel method to tailor the porous structure of KOH-activated biochar and its application in capacitive deionization and energy storage," *Biomass and Bioenergy*, vol. 87, pp. 107-121, 2016.
- [14] D. Tashima, E. Yamamoto, N. Kai, D. Fujikawa, G. Sakai, M. Otsubo, et al., "Double layer capacitance of high surface area carbon nanospheres derived from resorcinol-formaldehyde polymers," *Carbon*, vol. 49, pp. 4848-4857, 2011.
- [15] D. Tashima, M. Taniguchi, D. Fujikawa, T. Kijima, and M. Otsubo, "Performance of electric double layer capacitors using nanocarbons produced from nanoparticles of resorcinol-formaldehyde polymers," *Materials Chemistry and Physics*, vol. 115, pp. 69-73, 2009.
- [16] D. Tashima, H. Yoshitama, T. Sakoda, A. Okazaki, and T. Kawaji, "Characteristics of powdered activated carbon treated with dielectric barrier discharge for electric double-layer capacitors," *Electrochimica Acta*, vol. 77, pp. 198-203, 2012.
- [17] D. Tashima, K. Kurosawatsu, Y.-M. Sung, M. Otsubo, and C. Honda, "Surface modification of nanoporous materials for electric double layer capacitors application," *Materials Chemistry and Physics*, vol. 103, pp. 158-161, 2007.
- [18] T. Yamasaki, T. Aki, M. Shinozaki, M. Taguchi, S. Kawamoto, and K. Ono, "Utilization of Shochu distillery wastewater for production of polyunsaturated fatty acids and xanthophylls using *Thraustochytrid*," *Journal of Bioscience and Bioengineering*, vol. 102, pp. 323-327, 2006.
- [19] S. Yokoyama and S. Tarumi, "Production and some properties of low-salt seasoning from Shochu distillery waste," *Journal of Bioscience and Bioengineering*, vol. 92, p. 200, 2001.
- [20] Y. Tanaka, A. Murata, and S. Hayashida, "Accelerated composting of cereal shochu-distillery wastes by actinomycetes : Yonemi Tanaka^{1*}, Akira Murata¹, and Shinsaku Hayashida² (Joint Research and Development Center, Saga University, Honjocho, saga 8401 and Department of Agricultural Chemistry, Kyushu University, Higashi-ku, Fukuoka 8122) *Seibutsu-kogaku* 73: 365–372. 1995," *Journal of Fermentation and Bioengineering*, vol. 80, p. 421, 1995.
- [21] S. Ueda, Y. Teramoto, R. Ohba, T. Ueki, K. Kimura, and S. Shiota, "Batchwise ethanol fermentation with shochu distillery waste," *Journal of Fermentation and Bioengineering*, vol. 72, pp. 270-273, 1991.
- [22] A. Yamashita, Y. Mori, T. Oshima, and Y. Baba, "Preparation of activated carbon with high surface area using crab shell and shochu waste and the development of methane storage technology," *Carbon*, vol. 76, p. 469, 2014.
- [23] S. Brunauer, J. Skalny, and E. E. Bodor, "Adsorption on nonporous solids," *Journal of Colloid and Interface Science*, vol. 30, pp. 546-552, 1969.
- [24] K. S. W. Sing, "The use of physisorption for the characterization of microporous carbons," *Carbon*, vol. 27, pp. 5-11, 1989.
- [25] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, et al., "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984)," *Pure and Applied Chemistry*, vol. 57, pp. 603-619, 1985.
- [26] J. H. de Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuvel, and T. J. Osinga, "Thet-curve of multimolecular N₂-adsorption," *Journal of Colloid and Interface Science*, vol. 21, pp. 405-414, 1966.
- [27] E. P. Barrett, L. G. Joyner, and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms," *Journal of the American Chemical Society*, vol. 73, pp. 373-380, 1951.
- [28] L. Khezami, A. Chetouani, B. Taouk, and R. Capart, "Production and characterisation of activated carbon from wood components in powder: Cellulose, lignin, xylan," *Powder Technology*, vol. 157, pp. 48-56, 2005.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 6, Issue 6, November 2017

- [29] Suhas, P. J. M. Carrott, and M. M. L. Ribeiro Carrott, "Lignin – from natural adsorbent to activated carbon: A review," *Bioresource Technology*, vol. 98, pp. 2301-2312, 2007.
- [30] B. Cagnon, X. Py, A. Guillot, F. Stoeckli, and G. Chambat, "Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors," *Bioresource Technology*, vol. 100, pp. 292-298, 2009.
- [31] W.-H. Chen and P.-C. Kuo, "Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis," *Energy*, vol. 36, pp. 6451-6460, 2011.
- [32] Q. Li, F. Liu, L. Zhang, B. J. Nelson, S. Zhang, C. Ma, et al., "In situ construction of potato starch based carbon nanofiber/activated carbon hybrid structure for high-performance electrical double layer capacitor," *Journal of Power Sources*, vol. 207, pp. 199-204, 2012.
- [33] S. Zhao, C.-Y. Wang, M.-M. Chen, J. Wang, and Z.-Q. Shi, "Potato starch-based activated carbon spheres as electrode material for electrochemical capacitor," *Journal of Physics and Chemistry of Solids*, vol. 70, pp. 1256-1260, 2009.

AUTHOR BIOGRAPHY



Daisuke Tashima He received his B.E degree in department of Electrical and Electronic Engineering from University of Miyazaki in 2003, and his Dr. degree from University of Miyazaki in 2007. After working as Researcher at Faculty of Agriculture, University of Miyazaki, and Research Assistant Professor at Interdisciplinary Research Organization, University of Miyazaki, became Assistant Professor at Department of Electrical Engineering, Faculty of Engineering, and Fukuoka Institute of Technology since April 2015. His research interest includes electric double layer capacitor and proton exchange membrane fuel cell.



Takuya Eguchi He received a bachelor's degree from the Fukuoka Institute of Technology in 2016, completed the first stage of the master program in 2017. His research interest is producing low-cost activated carbons from shochu waste for electrical double layer capacitors using aqueous electrolyte.



Takashi Kumamoto He received a bachelor's degree from the Fukuoka Institute of Technology in 2016, completed the first stage of the master program in 2017. His research interest is producing low-cost activated carbons from shochu waste for electrical double layer capacitors using organic electrolyte.



Masumi Fukuma He received B.E and M.E degree in department of Electrical and Electronic Engineering from Toyohashi University of Technology in 1983 and 1985, respectively. He belonged to the Optical fiber division in Sumitomo Electric Industries from 1985 to 1992. He received Dr. degree from Toyohashi University of Technology in 1997. He became lecturer form 1992 in department of Electrical Engineering of Matsue College of Technology in Shimane, Japan, where he is currently professor. His main research interests are space charge measurement techniques in dielectrics and electric double layer capacitors.



Seiji Kumagai He received his B.E degree in department of Electrical and Electronic Engineering from Akita University in 1995, and his Dr. Degree from Akita University in 2000. He is now associate professor of Akita University. His research interest includes power storage devices and electrical insulating materials.