



Short communication

## Converting rice husk activated carbon into active material for capacitor using three-dimensional porous current collector

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### ABSTRACT

We have successfully applied rice husk activated carbon (RHAC) as an active material for the electric double layer capacitor using a three-dimensional (3D) porous current collector. The capacity and cycle stability were evaluated in a 1.0 mol dm<sup>-3</sup> tetraethylammonium tetrafluoroborate/propylene carbonate solution in the range of 0–2.5 V. The specific capacity of the RHAC was about 14 mAh g<sup>-1</sup> at the 50 mA g<sup>-1</sup> discharge rate, corresponding to 19 F g<sup>-1</sup> under the present conditions. The RHAC cell using the 3D porous current collector possessed a lower internal resistance and better high-rate discharge properties than the RHAC cell using a conventional aluminum (Al) foil collector. After 5000 cycles of charging and discharging, the RHAC cell with the 3D current collector maintained 95% of its initial capacity, while the capacity of the one with the Al foil collector dropped to only 30%.

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### 1. Introduction

Rice grain, when threshed, leaves 20% of its weight as the husk, a major agricultural waste in the world [1]. On average, the rice husk is composed of 22% lignin, 38% cellulose, 18% hemicelluloses, 2% extractive, and 20% ash [2]. Unlike other grains, the husk of gramineous plants, to which rice belongs, is characterized by this high ash content. The ash, most of which is silica, renders the rice husk unsuitable as a raw material for animal feed. It is also not useful for soil improvement because of the lignin content that defies biological degradation. Due to its low-value applications in the agricultural area, more than 120 million metric tons of rice husks are dumped as waste every year around the world [3].

In order to beneficially make use of the rice husk, attempts have been made to process the rice husk into industrial carbon materials [4–8]. Industrial carbon materials, such as high thermal conductive carbon fibers [9,10], carbon electrodes [11–13] and activated carbon fibers [14–16], are usually produced from petroleum pitch, a typical non-renewable fossil fuel resource. On the other hand, rice husk is a renewable and abundant biomass resource available around the world. Facing rising oil prices and the volatile availability of fossil resources, we can consider rice husk as a viable option to create carbon materials.

In this study, we focused on the rice husk activated carbon (RHAC) as an active electrode material for capacitors. The silica component contained in the RHAC increases from 20% to 50% of the total mass during the activation process [17], resulting in poor electrochemical properties such as a low electronic conductivity. Guo et al. reported that the electrochemical performance of RHAC was improved when the silica was removed from the rice husk, though at the expense of a laborious removal process [18].

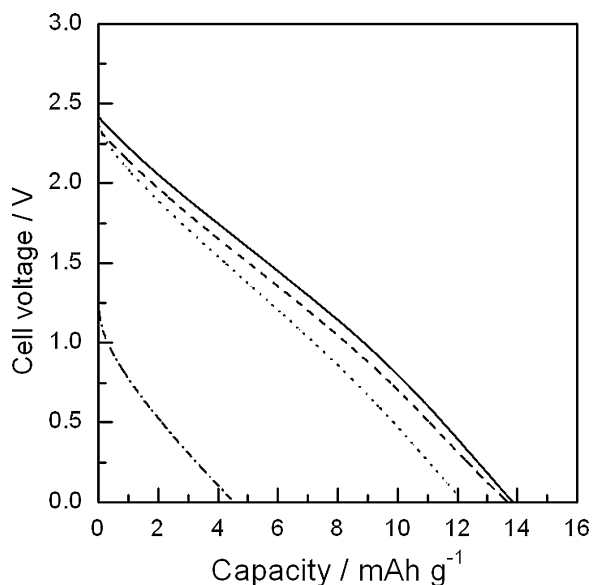
The aim of this study is to improve the poor electrochemical performance of the RHAC without removing the silica. We applied the methodology proposed by Yao et al. who had previously revealed that the three-dimensional (3D) current collector improved the power output properties in an electric double layer capacitor (EDLC) based on a pitch-based activated carbon [19]. We examined the rate performance and cycle stability of the EDLC made of the 3D current collector and RHAC.

### 2. Experimental

The RHAC used in this study was prepared by Associate Professor Seiji Kumagai (Akita Prefecture University) using the CO<sub>2</sub>-activation method [17]. The RHAC consists of 50 wt% carbon and 50 wt% silica. The specific surface area of the RHAC is 770 m<sup>2</sup> g<sup>-1</sup>. As the 3D current collectors, two types of Celmet<sup>®</sup> (Sumitomo Electric Industries, Ltd.), a nickel–chromium substrate and a foam nickel substrate, were used for the positive and negative electrodes, respectively. The weight per geometric area, thickness, porosity and

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**Fig. 1.** The discharge curves of the 3D cell (---: at  $50 \text{ mA g}^{-1}$ , ...: at  $1000 \text{ mA g}^{-1}$ ) and Al foil cell (—: at  $50 \text{ mA g}^{-1}$ , -·-: at  $1000 \text{ mA g}^{-1}$ ).

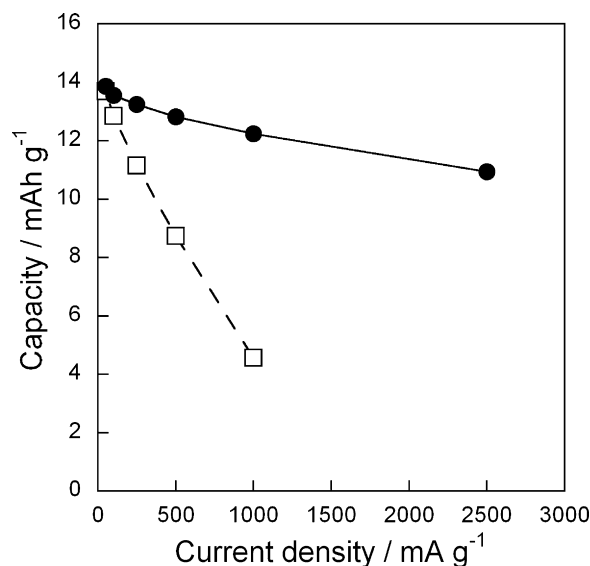
specific surface area of the nickel–chromium Celmet are  $450 \text{ g m}^{-2}$ , 1.4 mm, 96% and  $0.2 \text{ m}^2 \text{ g}^{-1}$ , respectively [19]. Those of the nickel Celmet are  $420 \text{ g m}^{-2}$ , 1.4 mm, 97% and  $0.19 \text{ m}^2 \text{ g}^{-1}$ , respectively [20].

For preparation of the electrodes, RHAC as the active material, ketchen black as the conductive additive, and polyvinylidene fluoride (PVdF) as the binder were mixed in the weight ratio of 84:10:6 in *N*-methyl-2-pyrrolidone (NMP). The obtained slurry was loaded into the Celmet 3D current collectors, which were then dried at  $80^\circ\text{C}$  and roll pressed, yielding an electrode with a  $170\text{-}\mu\text{m}$  thickness. For comparison, we prepared a conventional thin film electrode with an aluminum foil current collector using the same slurry (electrode thickness:  $80\text{-}\mu\text{m}$ ). The amounts of RHAC on the 3D current collector and on the Al foil were 7.6 and 4.2 mg per square centimeter of geometrical area of the electrode, respectively. In this paper, we denote the cell prepared using the 3D current collector and the Al foil current collector as the 3D cell and the Al foil cell.

Two-electrode cells of  $2 \text{ cm} \times 1.5 \text{ cm}$  were assembled for the electrochemical tests. A cellulose-type nonwoven cloth with a  $60\text{-}\mu\text{m}$  thickness was used as the separator. The cell was sealed after adding the electrolyte,  $1.0 \text{ mol dm}^{-3}$  tetraethylammonium tetrafluoroborate in propylene carbonate. The charge–discharge tests were performed using a computer-controlled charge/discharge system (BSL series, Keisokuki Center Co., Ltd.) between 0 and 2.5 V. In the present study, the mass appearing in the denominator of the current density “ $\text{mA g}^{-1}$ ” or the energy density “ $\text{mAh g}^{-1}$ ” is defined by the mass of carbon content in the RHAC, i.e., the mass of RHAC subtracted by the mass of silica. The cells were charged at a current density of  $200 \text{ mA g}^{-1}$  and discharged at current densities ranging from 50 to  $2500 \text{ mA g}^{-1}$ . All measurements were performed at  $25^\circ\text{C}$ .

### 3. Results and discussion

Fig. 1 shows the discharge curves of the 3D cell and the Al foil cell measured at two current densities, i.e.,  $50 \text{ mA g}^{-1}$  and  $1000 \text{ mA g}^{-1}$ . At the discharge current density of  $50 \text{ mA g}^{-1}$ , the RHAC in either cell showed a similar discharge capacity,  $14 \text{ mAh g}^{-1}$ , which indicated that the difference in the current collector had no significant influence on the specific capacity of RHAC at this low discharge current



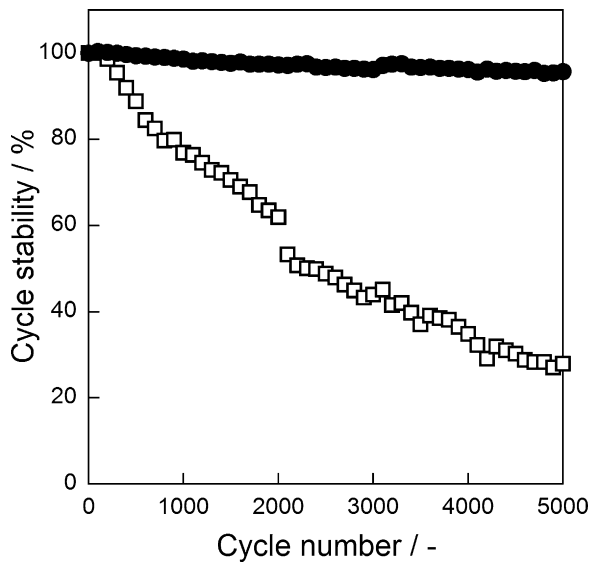
**Fig. 2.** The discharge current density dependence of the specific capacity for the 3D cell (—●—) and Al foil cell (—□—).

density. The specific capacity of  $14 \text{ mAh g}^{-1}$ , which corresponds to  $19 \text{ F g}^{-1}$  under the present conditions, is about a half the capacity of the pitch-based activated carbon electrode prepared in a manner similar to the present study [19]. This observation can be explained by the fact that the surface area per mass of carbon content in the RHAC, which is about  $1500 \text{ m}^2 \text{ g}^{-1}$ , is also about half that of the pitch-based activated carbons. In other words, the electrochemical capacity of the RHAC is comparable to that of the pitch-based activated carbons, if evaluated in terms of specific surface area or mass of carbon in the RHAC.

During the  $1000 \text{ mA g}^{-1}$ -discharging of the Al foil cell, a large ohmic loss was observed from which the internal resistance was estimated to be  $1.1 \Omega \text{ g}$ , or in terms of area of electrode  $262 \Omega \text{ cm}^2$ . In contrast, based on the discharge curve of the 3D cell, the internal resistance was about  $5.2 \times 10^{-2} \Omega \text{ g}$  ( $6.8 \Omega \text{ cm}^2$ ), indicating that the internal resistance of the cell can be drastically reduced using the 3D collector.

The dependence of the specific capacity on the discharge current density for the 3D cell and the Al foil cell is presented in Fig. 2. At the current density of  $1000 \text{ mA g}^{-1}$ , whereas the capacity of the Al foil cell significantly decreased to merely  $4.5 \text{ mAh g}^{-1}$ , the 3D cell generated a capacity of  $12 \text{ mAh g}^{-1}$ , which is 86% of the capacity observed at  $50 \text{ mA g}^{-1}$ , i.e.,  $14 \text{ mAh g}^{-1}$ . Even at the current density of  $2500 \text{ mA g}^{-1}$ , the 3D cell still delivered  $10 \text{ mAh g}^{-1}$  or 71% of  $14 \text{ mAh g}^{-1}$ .

To obtain a cell with large capacity, it is effective to prepare thick electrodes containing a large amount of active materials. To do this, however, the amount of binder to fix the active materials on the current collector becomes large compared with a thin electrode. The addition of the binder can cause the increase in the internal resistance of the electrodes because the binder is an electrically resistive component. In our case, the internal resistance of the 3D cell is much lower than that of the Al foil cell, despite the twofold thicker electrode in the former than in the latter. Several groups have succeeded in decreasing the internal resistance by increasing the contact area between the active material and the electron conductive path [21,22]. For example, Portet et al. prepared a carbon nanotube (CNT)-coated Al foil to increase the contact area and used it as a current collector for the EDLC [22]. They achieved a 25% decrease in the internal resistance of the cell compared to the cell assembled using the Al foil collector without the CNT coating. In our



**Fig. 3.** The relationship between the retention of the 3D cell (●), Al foil cell (□) and cycle number.

case, the 3D current collector has an order of magnitude higher surface area than the Al foil collector, which should lead to the higher contact area with the active material, and consequently, reduce the internal resistance in the 3D cell to a twentieth of that of the Al foil cell ( $5.2 \times 10^{-2}$  vs.  $1.1 \Omega \text{ g}$ ).

The result of the 5000-cycle test for the 3D cell and the Al foil cell is shown in Fig. 3. The charge–discharge test was carried out using the fixing current per the geometrical electrode area ( $1 \text{ mA cm}^{-2}$ ).

We define the cycle stability by

$$\text{Cycle stability (\%)} = \frac{C_n}{C_1} \times 100$$

where  $C_n$  and  $C_1$  are the capacities observed at the  $n$ th and 1st cycles, respectively. The Al foil cell using a pitch-based activated carbon prepared by Yao et al. exhibited a cycle stability similar to the 3D cell, i.e., both cells retained 92% after 1000 cycles [19]. For the RHAC, on the other hand, while the capacity of the Al foil cell dropped to 30% after 5000 cycles, the 3D cell achieved greater than a 95% cycle stability. The presence of silica in the RHAC probably gives rise to the fragility of the Al foil electrode made with RHAC, of which the detailed mechanism is still under investigation. The 3D current collector is remarkably effective in avoiding the otherwise poor cycle stability of the RHAC capacitor.

#### 4. Conclusion

We proved the viability of using a 3D porous current collector to overcome the poor rate properties and short cycle life of the RHAC as the active materials of an EDLC. The 3D porous current collector produced a low cell internal resistance, which is the reason for maintaining a high discharge capacity of the cell at a high current density discharging. The electrodes were able to withstand thousands of cycles using the 3D porous current collector. The 3D porous current collector will be applicable to cover up the inferior properties of the active materials for electrodes other than the RHAC.

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