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High-capacity carbons for lithium-ion batteries prepared from rice husk

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Abstract

We have prepared carbon anode materials by pyrolysis of rice husk (RH). Through X-ray powder diffraction, Brunauer–Emmett–Teller (BET) measurement, and ICP-AES analysis, the effects of acid–base pre-treatment, pyrolysis temperature, and the use of a proprietary pore-genic agent on the cell capacity of these materials were investigated. The carbonaceous materials made from RH treated with a proprietary agent showed an extraordinarily high reversible capacity of 1055 mAh/g. To our best knowledge, this new hard carbon material possesses the highest reversible capacity ever reported for any carbon anode materials of lithium-ion batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: High-capacity carbon; Lithium-ion batteries; Rice husk

1. Introduction

The search for low-cost and high-capacity carbon anode materials is now arousing interest worldwide, stimulated by increasing demand for lithium-ion batteries used to power portable electronic devices such as notebook computers and phones [1] and for vehicle propulsion in zero-emission vehicles (ZEVs) [2]. High-capacity carbons refer to materials with capacities greater than that of graphite (372 mAh/g). Several series of hard carbons used as anodes of lithium-ion batteries have been prepared by pyrolysis of natural or agricultural precursors such as sugar [3–5], cotton [6] and coffee beans [7]. The capacity of such materials is critically dependent on pyrolysis conditions and precursor sources. To lower the cost of raw materials, the selection of precursor has been shifted to natural or agricultural residues in this work.

Rice husk (hereafter abbreviated as RH) is a form of agricultural biomass and a major by-product in the rice milling industry. The estimated world-wide RH production was about 100 million tons according to a 1996 report by the Food and Agricultural Organization [8]. Disposal of such vast amounts of RH has been one of the main problems facing the rice milling industry. The traditional method of economical disposal, namely burning, faces growing public opposition and legal regulation. The utilization and management of rice crop residues has received more attention over

many years from those both inside and outside the field of agriculture.

The major constituents of RH are silica (20–25%) and cellulose, which yields carbon when pyrolyzed under inert atmosphere [9]. Silicon-doped hard carbons were reported to improve cell capacity and cycle behavior [10,11]. Accordingly, we consider RH to be a potentially good low-cost source for high-capacity amorphous carbon containing micro-amounts of silicon.

The main objectives of this preliminary work are: (a) to develop a procedure for preparing high-capacity hard carbon from RH; (b) to optimize the process variables such as pyrolysis temperature and pore-genic agents; (c) to attempt preparation of hard carbons with high surface area and well-developed porosity by carbonization with pore-genic agents.

2. Experimental

The raw material, RH obtained from a local rice mill, was thoroughly washed with water to remove adhering soil and clay, and dried at 110°C in an oven overnight. The dried husk (ca. 30 g) was refluxed with 400 ml of 3N HCl solution for 1 h. After leaching, the husk was thoroughly washed with distilled water until the filtrate was free from acid. The leached husk was then dried at 110°C for 2 h. After drying, the husk was first transferred into a quartz tube, which was then purged with argon for 30 min. The tube was initially heated at 150°C for 1 h to remove water from the husk and then heated at a 5°C/min rate to reach pyrolysis temperature

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(from 500 to 900°C) for another hour. The black residues (about 8 g) were ground as carbon product. In the case of base treatment, the acid-free husk was refluxed with 400 ml of NaOH solution (0.1, 0.3, or 4N) for 1 h. After leaching, the husk was washed with distilled water until the filtrate was free from base and the process continued following the normal procedure as described above. When a pore-genic agent was used, the husk was immersed in the solution of the agent for 1 day with sufficient stirring. After pyrolysis, the carbonaceous product was then treated with 3N HCl solution to remove metallic ingredients present in the RH.

Powder XRD measurements were made with a Siemens D-500 diffractometer equipped with a diffracted beam monochromator including D-5000 data treatment software and Cu K α radiation of 1.5406 Å. The sample was set up on a glass holder in the diffractometer. Data were collected between 5 and 80° (2θ) at a 0.05° resolution. The specific surface area of the carbon sample was measured by nitrogen gas adsorption and the Brunauer–Emmett–Teller (BET) calculation in a Micromeritics ASAP-2010 surface analyzer. A mixture of 30 mol% (m/o) nitrogen in 70 m/o helium was used as a carrier gas. The hydrogen and carbon contained in the disordered carbons were measured with a Heraeus CHN-rapid elemental analyzer.

Carbon electrodes were fabricated on a weight basis of 90% carbon, 8% polyvinylidene fluoride (PVDF) and 2% carbon black (added to enhance the electronic conductivity). Excess NMP was used until the paste achieved a smooth syrupy viscosity. The paste was then spread uniformly on copper foil and NMP evaporated at 110°C for about 1.5 h. The coated foil was compressed into 110–130 μm . Then, the foil was cut into a circle with a diameter of 13 mm. Coin-type-2325 cell hardware used for the cycling tests was similar to that described in [12]. A microporous film (Celgard 3501 as the separator) wetted with electrolyte (1 M LiPF₆ dissolved in a 50/50 v/v% mixture of EC and DEC) was sandwiched between the carbonaceous cathode and lithium foil anode. The coin cell assembly was carried out in an argon-filled glove box where both moisture and oxygen concentration were about 1 ppm. A Maccor S-4000 Battery Test System controlled the cell cycling tests. The cells were first discharged using a constant current of 37.2 mA/hg (0.1°C rate) until the voltage dropped to 0.005 V (versus lithium metal), then the cells were charged to 3 V.

3. Results and discussion

Table 1 describes the RH carbon samples prepared in this preliminary work, and contains the following items: (a) the sample code, (b) pyrolysis temperature, (c)–(e) process variables such as the use of acid, base and pore-genic agent, (f)–(h) XRD results, (i) H/C atomic ratio, (j) silicon content, (k) BET surface area, and (l) reversible capacity. The pyrolyzing temperature, T_{pyr} , was changed from 500 to

900°C to obtain an optimum or practical temperature, which would result in the largest capacity for lithium in RH carbons. Three series of carbon samples were prepared with the use of acid, base and pore-genic agent. The d_{002} value is the interlayer distance between graphene sheets. The empirical parameter, R , is defined in [13], and measured as the ratio of the peak count rate at the (0 0 2) peak divided by the background level at the same angle. It is used to estimate the fraction of single-layers in hard carbon samples randomly positioned among groups of single-layers, bilayers and trilayers. The value of R depends on the single layer fraction. Liu et al. indicated that samples with lower R , having more single layers, generally gave larger specific capacities. The hydrogen to carbon atomic ratio of the samples (H/C atomic ratio) was calculated by taking the ratio of hydrogen to carbon weight percentages (obtained from the results of CHN elemental analysis) and multiplying by 12 (carbon atomic weight). Zheng et al. showed that large hysteresis is highly correlated to the high hydrogen content or H/C atomic ratio [14].

The XRD patterns of the RH carbons pyrolyzed in the temperature range between 500 and 900°C are shown in Fig. 1. All the peaks have broad shapes indicating highly disordered carbons [15]. Only the (0 0 2) Bragg peak due to the stacking of carbon layers appears significant. The profile of the (0 0 2) peak of these materials changes little as the temperature is increased. However, the interlayer distance (d_{002}) increases with increasing pyrolysis temperature. As listed in Table 1, the interlayer distance increases from 3.770 Å for carbon pyrolyzed at 500°C to 4.100 Å for carbon pyrolyzed at 900°C. The increase in d_{002} may be ascribed to the introduction of some interstitial atoms into the initial pristine graphite structure [16]. Since silica is one of the major constituents (20–25%) in RH, silicon could be the interstitial atoms between the aromatic planes of carbon atoms. In this work, the quantitative results from inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) analysis indicated that the silicon content in our carbon products without any base treatment pyrolyzed between 500 and 900°C was about 15–16%, whereas the silicon content in the carbon products with base treatment at various NaOH concentrations pyrolyzed at 700°C was less than 0.01% beyond the detection limit of ICP-AES method. The H/C atomic ratio decreases monotonically for each of the samples as they are heated. For instance, the H/C atomic ratio decreases from 0.68 to 0.31 as the pyrolysis temperature increased from 500 to 900°C.

Fig. 2 displays XRD patterns of the RH-based carbons pyrolyzed at 700°C. Prior to pyrolysis, the precursors of these carbon samples were treated with various concentrations (0.1, 0.3, or 4N) of NaOH solutions to remove silica from RH. The d_{002} values of RHC06 to RHC08 in Table 1 show that the interlayer distance decreases with increasing NaOH concentration. This is good evidence that the decrease in silicon content due to the treatment of high NaOH concentration results in a decrease in d_{002} . The

Table 1
Summary of the samples prepared from rice husk in this work

| (a) Sample | (b) T_{pyr} (°C) | (c) Acid leaching (3N HCl) | | (d) NaOH (N) | (e) Pore-genic agent ratio | (f) 2θ (0 0 2) | (g) d_{002} (Å) | (h) X-ray ratio (R) | (i) H/C atomic ratio | (j) Si content (%) | (k) Surface area (m ² /g) | (l) Capacity (mAh/g) | | | |
|------------|------------------------------|-------------------------------|--------------------|-----------------|-------------------------------|--------------------------|----------------------|----------------------------|-------------------------|-----------------------|---|----------------------|------|-------------------|-------------------|
| | | Prior to pyrolysis | After pyrolysis | | | | | | | | | First cycle | | Tenth cycle | |
| | | | | | | | | | | | | D | C | D | C |
| RHC01 | 500 | v | – | – | – | 23.58 | 3.770 | 1.67 | 0.68 | 14.8 | 199 | 7 | 2 | 2 | 2 |
| RHC02 | 600 | v | – | – | – | 23.46 | 3.789 | 2.24 | 0.53 | 15.7 | 277 | 605 | 279 | 235 | 238 |
| RHC03 | 700 | v | – | – | – | 22.41 | 3.964 | 2.02 | 0.48 | 15.9 | 277 | 691 | 320 | 289 | 279 |
| RHC04 | 800 | v | – | – | – | 21.75 | 4.083 | 2.07 | 0.46 | 15.0 | 294 | 637 | 279 | 240 | 234 |
| RHC05 | 900 | v | – | – | – | 21.66 | 4.100 | 2.34 | 0.31 | 16.2 | 205 | 207 | 89 | 131 | 128 |
| RHC06 | 700 | v | 0.1 | – | – | 23.05 | 3.855 | 1.96 | 0.46 | | 267 | 444 | 165 | 134 | 132 |
| RHC07 | 700 | v | 0.3 | – | – | 23.31 | 3.813 | 1.88 | 0.34 | | 371 | 819 | 463 | 293 | 292 |
| RHC08 | 700 | v | 4 | – | – | 23.37 | 3.803 | 1.85 | 0.32 | <0.01 | 404 | 571 | 354 | 265 | 261 |
| RHC09 | 500 | | v | 1:1 | – | 23.04 | 3.857 | 1.92 | 0.45 | | 1296 | 1190 | 457 | 608 ^a | 554 ^a |
| RHC10 | 500 | | v | 1:3 | – | 23.68 | 3.754 | 2.00 | 0.42 | | 1597 | 2259 | 853 | 858 ^a | 793 ^a |
| RHC11 | 500 | | v | 1:5 | – | 23.95 | 3.713 | 2.10 | 0.37 | | 1403 | 2374 | 1055 | 1128 ^a | 1051 ^a |

^a Data were taken at the end of the fifth cycle; D: discharge; C: charge.

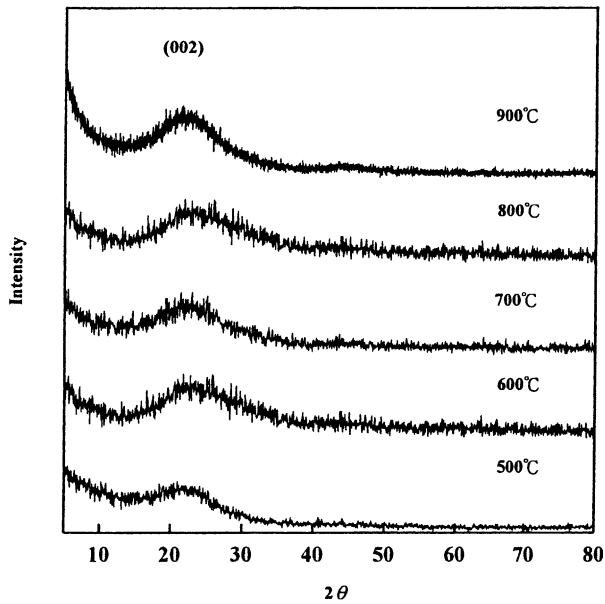


Fig. 1. XRD patterns of RH carbons pyrolyzed at various temperatures.

effect of NaOH treatment on d_{002} is clearly seen in the fact that the interlayer distance decreases from 3.964 Å without base treatment to 3.855–3.803 Å with base treatment. The H/C atomic ratio decreases slightly after base treatment, especially in higher concentrations.

The effect of T_{pyr} from 500 to 900°C on the capacity of Li/carbon coin cells was studied. The voltage profiles of these samples are shown in Fig. 3, except for the RHC01 sample pyrolyzed at 500°C which showed virtually no capacity as indicated in Table 1. The optimum T_{pyr} was 700°C in terms of the discharge and charge capacity of the first cycle, 691 and 319 mAh/g, respectively. The reversible capacity was about

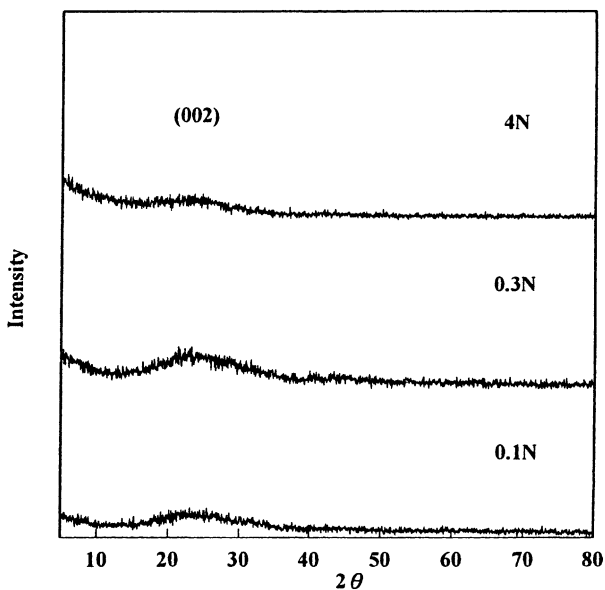


Fig. 2. XRD patterns of RH carbons treated with various concentrations of NaOH solutions prior to pyrolysis.

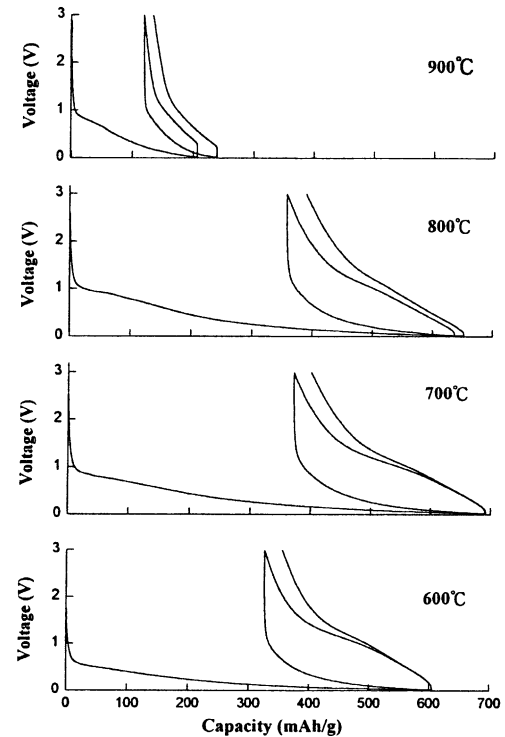


Fig. 3. Voltage profiles for cells with RH carbon samples pyrolyzed at various temperatures.

280 mAh/g at the tenth cycle. During the base treatment, only samples refluxed with NaOH at higher concentrations made slight improvements in capacity. The voltage profiles are shown in Fig. 4.

When pretreated using a proprietary pore-genic agent of a higher concentration prior to pyrolysis, the resulting hard carbon products (RHC10 and RHC11) showed a tremendous

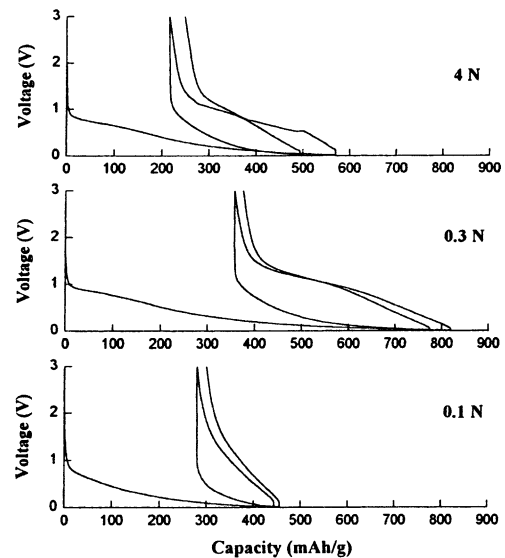


Fig. 4. Voltage profiles for cells with RH carbon samples treated with various concentrations of NaOH solutions prior to pyrolysis.

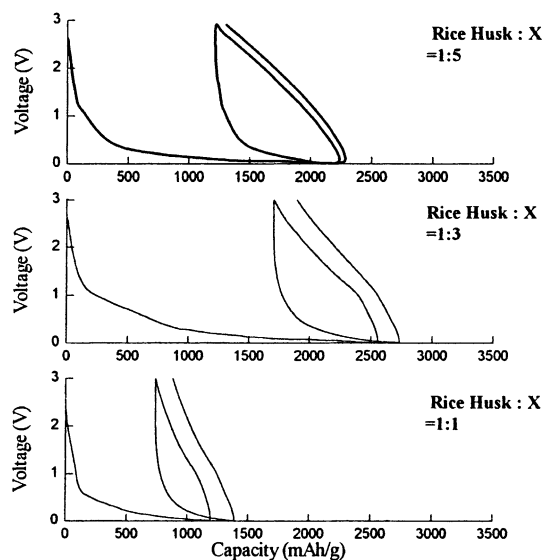


Fig. 5. Voltage profiles for cells with RH carbon samples treated with a proprietary pore-genic agent at various weight ratios of rice husk to the agent.

increase in cell capacity. Fig. 5 displays the voltage versus capacity for Li/carbon cells containing RHC09, RHC10, and RHC11 samples, whose raw husks were pretreated, prior to pyrolysis, in a solution of a weight ratio of RH to pore-genic agent, 1:1, 1:3, and 1:5, respectively. As listed in Table 1, the cell capacity of these samples increases with an increase in the weight ratio of RH to pore-genic agent. Interestingly, the use of a pore-genic agent results in a significant increase in surface area or the number of micropores. Based on BET analysis, surface area of raw RH carbons without any treatment was about $20 \text{ m}^2/\text{g}$, whereas surface area of RH carbons with pore-genic treatment was at least $1200 \text{ m}^2/\text{g}$ as shown in Table 1. The first discharge and charge capacity

values of RHC11 were 2374 and 1055 mAh/g, respectively. At the fifth cycle, the reversible capacity remained at 1051 mAh/g. To our best knowledge, both irreversible and reversible capacity values are the highest ever reported for any carbon anode materials of lithium-ion batteries. Even though the irreversible capacity of RHC11 was very high and not practical at this early stage, we believe that there is enormous potential for future work on these new super hard-carbon materials.

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