

Pyrolytic Carbons from Acid/Base-Treated Rice Husk as Lithium-Insertion Anode Materials

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Abstract—Lithium insertion characteristics of high-capacity disordered carbons derived from rice husk are described. The carbonaceous materials were synthesized by pyrolyzing rice husk under argon with and without prior treatment with a proprietary porogenic agent. The high capacities of these disordered carbons are attributed to lithium that bound to the hydrogen-saturated carbons and also onto extra surfaces of the single layers of carbon. Other contributing factors are the accommodation of additional lithium in the nanoscopic cavities, interaction of lithium with surface functional groups, and lithium plating on the carbon surface. Although disadvantaged by high first-cycle irreversible capacities, the carbons derived from porogen-treated precursors delivered high capacities at increasing coulombic efficiencies as the cycling proceeded. The consistently high capacities and the ability of the carbons to sustain high-rate cycling make them potential candidates as anode materials for lithium-ion batteries.

Keywords- lithium-ion batteries; carbonaceous anode; pyrolytic carbons; high-capacity carbons; lithium insertion; rice husk; porogen

I. INTRODUCTION

Carbonaceous materials manifest themselves in a variety of crystallographic and morphological forms. Apart from the hundreds of industrial varieties, several carbonaceous materials have been synthesized in the laboratory, often by the pyrolysis of organic precursors. Although all forms of carbons can insert lithium, the extent of lithium intake and the reversibility of the reaction are determined by their lattice arrangement, surface texture, surface functional groups, etc. [1]. Pyrolytically derived carbons have a disordered structure and often contain substantial amounts of hydrogen. These carbons have demonstrated lithium insertion capacities much larger than the 372 mAh/g theoretically possible with perfectly graphitic structures [2, 3]. However, the high irreversible capacities of these carbons [4] even after several cycles [5] and the large hysteresis in the charge-discharge profiles of hydrogen-containing carbons [6] continue to be major disadvantages. Despite these shortcomings, disordered carbons are pursued for their potential applicability in practical devices.

In addition to their advantages of high lithium intake capacities and good cyclability, disordered carbons can be structurally modified by varying the nature of their organic

precursors and temperature protocols. Disordered carbons obtained by pyrolysis of organic precursors contain a predominantly planar hexagonal network of carbons, but lack extended crystallographic ordering. Pyrolytic carbons have also been known to retain up to 30 at. % of residual hydrogen [7]. The high lithium capacities in pyrolytically prepared carbon varieties have been found to be associated with both disorder [8] and hydrogen content [9]. Although several models have been proposed to account for the additional capacity exhibited by disordered carbons [10], no model is able to satisfactorily account for the simultaneous large capacities and the voltage hysteresis in highly porous carbons with H/C ratios of less than 0.05 [11]. The absence of long-range order frustrates attempts at understanding the structure-reversible lithium intercalation properties of these carbons.

Among the cheapest and most abundant precursors for disordered carbons are biomass materials like sugar [12], cotton wool [13], rice husk [14], starch and oak [15], walnut and almond shells [15], and peanut kernels [16]. Fey et al. [16] reported that peanut kernel-derived carbons delivered first-cycle insertion capacities as high as 4765 mAh/g, the highest lithium intake capacities reported so far. It is also noteworthy that disordered carbons derived from rice husk maintained good reversibility upon repeated cycling, the first and fifth-cycle deinsertion capacities being 1055 and 1051 mAh/g, respectively [14]. In this paper, we report the results of our study on the structural, morphological and electrochemical features of rice husk-derived carbons.

II. EXPERIMENTAL

Carbon samples for this work were synthesized as described elsewhere [14]. Cleaned and dried rice husk was stirred for 24 h with an aqueous solution of a proprietary porogenic agent and dried. The amount of porogen used was such that the weight ratios of the rice husk to the porogen were 1:1, 1:2, 1:3, 1:4 and 1:5 (hereinafter referred to as P = 1, 2, 3, 4 and 5, respectively). The porogen-treated rice husk samples were then heated at 150°C for 1 h, followed by a 1-h calcination at 500, 600, 700, 800 and 900 °C. The calcined samples were refluxed in HCl, washed till the pH of the washing was 7, dried, and ground into fine powders. The sample (P=1, calcined at 600 °C) was denoted as C-1-600, and the rest may be deduced by analogy.

III. RESULTS AND DISCUSSION

A. Thermal analysis

The TG and DTA curves recorded with the porogen-free and porogen-treated ($P = 5$) rice husk samples between room temperature and 900 °C are shown in Fig. 1 and Fig. 2. The endotherm and the corresponding weight loss centered around 100 °C in Fig. 1 are due to the loss of superficial moisture and other light volatiles from the husk. In their studies on the thermal degradation of rice husk in nitrogen, Mansaray and Ghaly [17] found that the active pyrolysis zone for rice husk was in the 184–380 °C range. This zone is attributed to the evolution of volatiles emanating upon decomposition of primary hemicellulose and cellulose [18]. Between about 400 and 500 °C, a major change in the slope of the TG curve can be seen. This region, known as the passive pyrolysis zone, indicates a second reaction zone, and is attributed to lignin conversion [18]. Further weight loss up to about 800 °C suggests that some reaction involving the char was continuing.

The differential thermogram shown in the inset has two weight loss regions, around 330 and 390 °C in the active pyrolysis zone. It has been reported [19] that hemicellulose decomposes mainly between 150 and 350 °C, cellulose between 275 and 350 °C, and lignin decomposes gradually between 250 and 500 °C. Thus, the first degradation step in the active pyrolysis zone involves the decomposition of hemicellulose and the initial decomposition stages of cellulose, while the second degradation step would involve the final stages of cellulose decomposition and the initial stages of lignin decomposition [17]. It must be noted that the temperature ranges for the decomposition reactions depend on the variety of rice husk as well as on the heating rate [17].

The TG and DTA patterns of the porogen-treated rice husk ($P = 5$) are shown in Fig. 2. It can be seen that the porogen decomposes in the active pyrolysis zone of rice husk, which is a critical factor in aiding the formation of pores. The extra heat generated by the decomposition of the porogen aids the sluggish formation and subsequent organization of the carbon layers. As in the porogen-free sample, the passive pyrolysis region is associated with further loss of volatile vapors and aromatic condensation processes that are part of the intricate pyrolytic reactions.

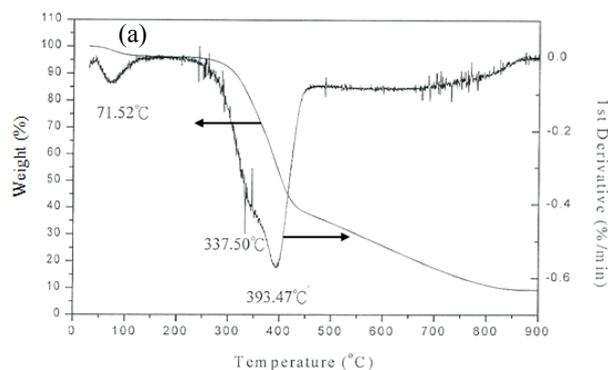


Figure 1. Thermal behavior of porogen-free in argon.

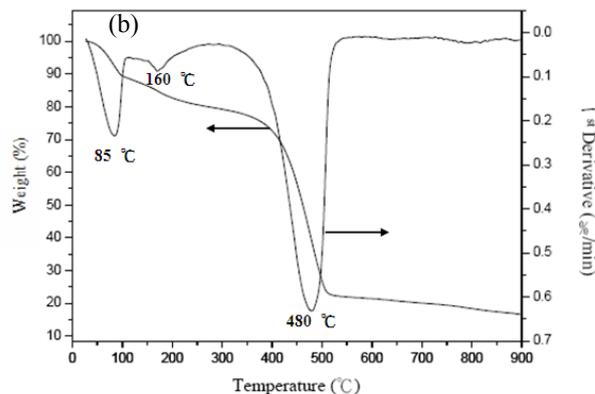


Figure 2. Thermal behavior of porogen-treated ($P = 5$) rice husk in argon.

B. Raman spectroscopy

Raman spectroscopy is a useful tool for the study of carbons because Raman spectral response is sensitive to the microscopic structure of the carbon. Raman spectra of the C-1-500, C-3-500 and C-5-500 carbons are shown in Fig. 3. Two bands can be seen in all the spectra: one, the D-band around 1355 cm^{-1} , and the other, the G-band around 1580 cm^{-1} . The G-band is an inherent Raman-active band for the ideal graphite structure, corresponding to the E_{2g} vibration mode [20], and ascribed to the C—C stretching in the longitudinal symmetry axis of the graphite plane [21]. The D-band, usually identified as the A_{1g} mode, is forbidden for the two-dimensional lattice of graphite according to selection rules, and is a subject of controversy [22]. However, for graphite crystallites of finite sizes, the A_{1g} mode will become Raman-active. This band is assigned to defects on the boundary of the carbon layers. The G-band also became sharper, indicating a high degree of graphitization in the products.

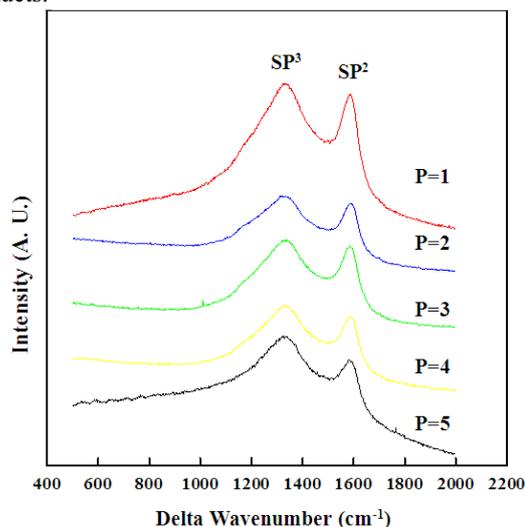


Figure 3. Raman spectra of the carbons obtained from rice husk precursors containing different porogen contents.

Table I shows the positions of the characteristic Raman bands and the integrated intensity ratios (ID/IG) of the carbon samples treated at 500 °C. Although the C-1-500 sample gave the highest individual peak intensities and seemingly contravened our assumption on the effect of porogen, the highest intensity ratio value was registered by the C-5-500 sample. The integrated intensity ratio is a measure of the orientation of the graphitic planes and the degree of graphitization [23].

TABLE I. POSITIONS OF THE CHARACTERISTIC RAMAN PEAKS AND THEIR INTEGRATED INTENSITY RATIOS

P	Peak (cm ⁻¹)	Integrated Area (A)	A _{SP3} /A _{SP2}
1	SP ³	1319.9	5812000
	SP ²	1584.6	
2	SP ³	1311.9	2955700
	SP ²	1586.6	
3	SP ³	1321.1	3218700
	SP ²	1580.5	
4	SP ³	1317.1	3329400
	SP ²	1586.1	
5	SP ³	1308.6	6580100
	SP ²	1588.1	

C. Galvanostatic charge-discharge studies

We have already shown [14] that C-0-500 was not electro-active, and that among the carbons derived from porogen-free precursors, the highest first-cycle insertion capacity was obtained with C-0-700, whose capacity was 691 mAh/g. The inactivity of C-0-500 is due to (i) the temperature being too low for sufficient carbonization-aromatization of the products, and (ii) the insignificant number of micropores, which are not retained once they are formed by the evolving gases. However, in carbons derived at temperatures above the carbonization temperature, the micropores formed can be retained. Any coalescence of the small pores to yield large ones may only serve to increase surface area, and disfavor their function as cavities in which lithium can be stored.

In contrast, the carbons derived from the porogen-treated rice husk were shown to be highly electro-active even when the pyrolysis temperature was maintained at 500°C. In fact, the first-cycle insertion capacities for C-1-500, C-2-500, C-3-500, C-4-500 and C-5-500 were 1190, 1584, 2259, 3253 and 2374 mAh/g, respectively. The corresponding irreversible capacities were 62, 66, 62, 69 and 56 %. Thus, the P = 5 sample was found to yield the highest deinsertion capacity and the lowest irreversible capacity. Therefore, a decision was made to study the effect of pyrolysis temperature on the capacity of carbons derived from the P = 5 precursors. As the pyrolysis temperature was raised to 600°C, the first-cycle insertion capacity rose to 2523 mAh/g (C-5-600). However, a further increase in temperature reduced the first-cycle insertion capacity: 2507, 1598 and 1530 mAh/g, respectively, for C-5-700, C-5-800 and C-5-900. The fact that the porogen-laden rice husks yielded carbons with higher capacities indicates that the decomposition of the porogen provided sufficient energy for the carbonization-graphitization processes. It is most obvious in the case of the carbons obtained at 500 °C. While the C-0-

500 material gave a paltry 7 mAh/g, the C-5-500 material could insert a remarkable 2374 mAh/g equivalent of lithium. Fig. 4 shows the deinsertion capacities of these carbons as a function of cycle number.

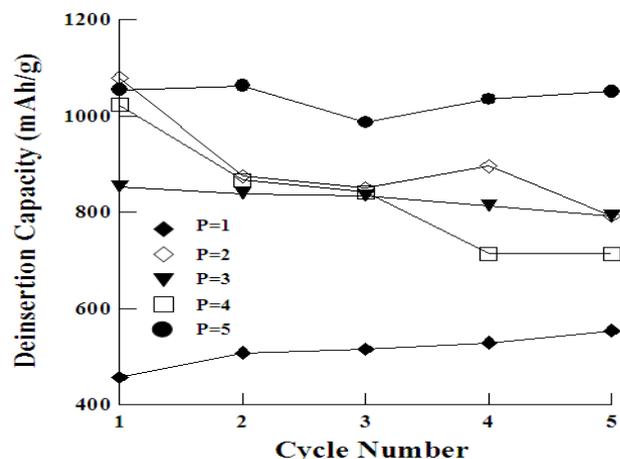


Figure 4. Deinsertion capacities of carbons obtained from porogen-treated (P = 5) rice husk as a function of cycle number.

The high first-cycle insertion capacities and the attendant irreversible capacities are attributed to the high H/C ratios of these low-temperature pyrolytic carbons [2, 4], as well as to the presence of a large number of nanopores [24]. According to Dahn et al. [2, 4] hydrogen-containing carbons show capacities proportional to their hydrogen content and exhibit large hysteresis. They suggest that such low-temperature carbons have an abundance of nanopores. It can be seen from Table II that the H/C ratio (0.37) is the highest for the carbon prepared at 500 °C. This ratio decreased gradually as the temperature was raised. The low resolution of the characteristic (002) reflections coupled with the small value of the R factor (2.10) suggest that these low-temperature carbons had a predominance of randomly stacked single layers of carbon that can provide double surfaces for lithium accommodation as well as nanopores that can lodge more lithium. The low R factors suggest that under their formation conditions, there was insufficient thermal energy for graphene layers to rotate into a parallel alignment in accordance with Dahn's 'falling cards model' [25]. Thus, the low-temperature carbons have a large number of non-parallel, unorganized single layers of carbon. The presence of such uncorrelated graphene fragments plays an important role in the amount of lithium that a carbon sample can insert [2]. As the formation temperature of the carbons is increased, the thermal energies reach values high enough to break the links between adjacent sheets and favor their alignment into parallel orientations. As a result, not only are more and larger domains of organized regions formed (increasing the value of the R factor), but larger pores are also formed. In accordance with this model, carbon samples prepared at higher temperatures should have fewer unorganized single layers of carbon and nanopores, which should account for the lower lithium storage capacities.

TABLE II. ELEMENTAL ANALYSIS DATA, AVERAGE INTER-LAYER SPACINGS AND R FACTOR VALUES OF THE DIFFERENT CARBONACEOUS PRODUCTS.

Sample name	Percentage composition				Average Interlayer distance (Å)	R-factor
	C	H	N	H/C		
C-1-500	68.94	2.58	1.65	0.45	3.857	1.92
C-2-500	71.09	2.32	2.24	0.39	3.822	2.51
C-3-500	70.16	2.43	2.41	0.42	3.754	2.00
C-4-500	67.79	2.18	1.90	0.39	3.753	2.24
C-5-500	67.48	2.07	1.96	0.37	3.713	2.10
C-5-600	73.35	1.76	0.72	0.29	3.720	2.10
C-5-700	67.51	1.55	0.58	0.28	3.751	2.60
C-5-800	66.37	1.38	0.57	0.25	3.696	2.64
C-5-900	65.05	1.16	0.55	0.21	3.695	2.68

For some of the carbons the deinsertion capacities were found to increase with cycling. It can also be seen that although the first-cycle irreversible capacity generally became lower with increasing pyrolysis temperature, a greater percentage was lost with increasing temperature. Interestingly, the coulombic efficiencies for the charge-discharge processes improved with cycling. Mention must be made of the high reversible capacities of the carbons, particularly of C-5-500. They were consistently much higher than the 372 mAh/g, the maximum theoretical capacity that can be tapped from perfectly graphitic structures. Thus, it appears that although the first-cycle irreversible capacities of the carbons were high, they were unique in that they continued to deliver high capacities. This is illustrated in Fig. 5, which presents the long-cycling behavior of C-5-700 at 0.1 and 0.2 C rates. Capacity was remarkably constant even beyond 150 cycles. Additionally, the ability of the carbon to sustain high-rate charge and discharge is also striking. Thus, if the first-cycle irreversible capacity loss in these carbonaceous materials can be suppressed, the porogen-treated rice husk carbons would be attractive anode materials for lithium-ion batteries.

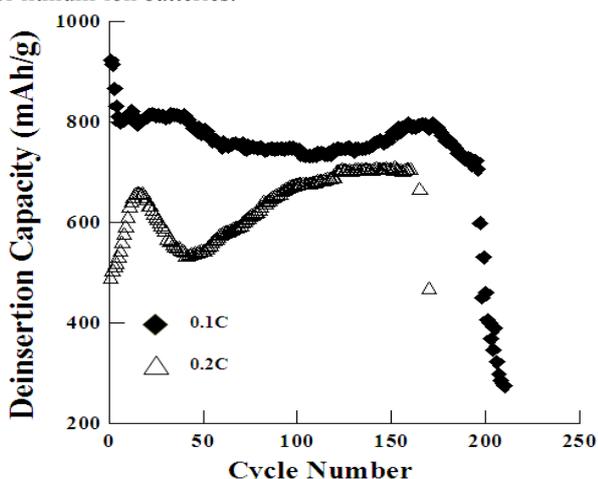


Figure 5. Cycling behavior of C-5-700 carbon at 0.1 and 0.2 charge-discharge rates. Voltage range: 3.000–0.005V.

IV. CONCLUSIONS

Prolytic carbons derived from porogen-treated rice husk have been shown to possess high lithium insertion capacities. The high capacities in these disordered carbons are believed to be due to the binding of lithium to the hydrogen-saturated carbons and onto the extra surfaces of the single layers of carbon. Although the first-cycle irreversible capacities of the carbons were high, they continued to deliver high capacities at increasing coulombic efficiencies as the cycling proceeded. The remarkably constant and high capacities and the ability of the carbons to sustain high-rate cycling make them potential candidates as anode materials for lithium-ion batteries.

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