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# High-capacity disordered carbons derived from peanut shells as lithium-intercalating anode materials

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# Abstract

We report for the first time initial lithium intake capacities for pyrolytic carbonaceous materials far exceeding even the theoretical value for metallic lithium. The carbonaceous materials were synthesized by pyrolysis of peanut shells under argon. Thermal conditions for the pyrolysis were optimized in order to obtain materials with desirable electrochemical properties. Peanut shells carbonized in a two-step process that occurred between 300 and 600 °C. The shells were also treated with a proprietary porogenic agent with the goal of altering the pore structure and surface area of the pyrolysis products. Both the untreated and the porogen-treated shells yielded carbons with poor crystallinity, although the surface area and the pore diameter of the latter registered a 66-fold and two-fold increase, respectively, over the former. Both the carbons had a predominance of non-parallel single sheets of carbons, as determined by the values of their *R* factors. Charge–discharge studies showed that although the capacities registered with carbons from the untreated shells varied with the H/C ratio, it was generally reasonable to relate the high initial capacities (in some cases as much as 4765 mAh/g) to the extra surface area of unorganized single layers of carbon and nanoscopic cavities generated by the pore-former. It is also believed that the 'extra' capacity may stem from lithium interaction with surface groups and from lithium plating on the carbon surface and subsequent passivation.

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# 1. Introduction

Successive improvements in faradaic capacity and cycle life, and improved safety characteristics have kindled renewed interest in lithium-intercalating carbonaceous anode materials for lithium-ion batteries. Lithium intercalated carbons have low working voltages (0–500 mV versus Li<sup>+</sup>/Li), show excellent reversibility for the lithium intercalation process, and maintain good dimensional stability during the topotactic charge–discharge processes. Graphitic carbons are the mainstay of anode materials in commercial lithium-ion cells today. This is despite the promise held by several disordered carbons with features like [1–4]: (i) higher uptake of lithium, often much higher than the theoretical limit of 372 mAh/g that perfectly graphitic structures can offer; (ii) their amenability to doctoring by varying the nature of their organic precursors and temperature

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protocols; and (iii) good cycling ability. 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 [4–6]. The high lithium capacities in pyrolytically prepared carbon varieties have been found to be associated with both disorder [7,8] and hydrogen content [1,4,9]. Several models have been proposed to account for the additional capacity exhibited by disordered carbons [4,5,10–13]. However, 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 <0.05 [14]. The absence of longrange order frustrates attempts at understanding the relationship between the structure and reversible lithium intercalation properties of these carbons.

Low-crystallized carbons prepared by pyrolysis of such condensed aromatics as pitch [7], poly-paraphenylene [5] and poly-acenic materials [2,3] have demonstrated capacities up to 700 mAh/g. Pyrolytic carbons have also been synthesized from a multitude of natural precursors, such as starch and oak [15], walnut and almond shells [15], lignin, cotton and wool [16], rice husk [17], and sugar [15,18–22].

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According to Xing et al. [22], who obtained capacities of about 650 mAh/g from sugar carbonized at 1050 °C, the electrochemical performance of carbons is largely determined by the pyrolysis conditions and surface morphology. While nanopores and voids in the carbon materials may facilitate greater accommodation of lithium [23–25], very large pores can be pejorative in that they can coaccommodate solvent molecules, resulting in extensive surface passivation. In this paper, we report the results of our work on the pyrolytic synthesis of carbons from peanut shells, and their structural and electrochemical intercalation characteristics.

# 2. Experimental

Carbon samples for this work were synthesized as described below. Good quality dry peanuts (from local sources) were pried open to obtain the shells. The shells were ground into a fine powder. Twenty grams of the powder was mixed with 100 g of a proprietary porogenic agent and stirred well for 24 h. The water in the mixture was allowed to evaporate at 110 °C over a period of 4 days. The dry sample was heated at a heating ramp of 10 °C/min in an argon atmosphere and was held at 150 °C for 1 h. Subsequently, the temperature of the sample was raised at a rate of 0.5, 1, 2.5 or 5 °C/min up to the desired temperature (between 500 and 800 °C), at which point it was held again for 1 h. After natural cooling to room temperature, the pore-former was removed by treatment in 3 N HCl followed by a 1 h heat treatment at 190 °C. The carbon sample without the porogenic agent was simply prepared by the heat treatment schedule above.

Elemental analysis was done on a Perkin Elmer CHN 2000 elemental analyzer. Powder X-ray diffractometry was performed (Siemens D 5000 X-ray diffractometer) with nickel-filtered Cu Ka radiation. The data were collected between scattering angles (2 $\theta$ ) of 5° and 80° in steps of 0.05°. A Sieko SSC 5000 TG/DTA equipment was used for thermal analysis. The analysis was done in argon between room temperature and 900 °C at a heating ramp of 10 °C/ min with a 50 mg sample. BET surface area measurements were carried out on a Micromeritics ASAP 2010 surface area analyzer. The microstructures of the carbonaceous products obtained with and without the porogen were examined by a JEOL JEM-200FXII transmission electron microscope equipped with an LaB<sub>6</sub> gun. The samples for TEM studies were prepared by dispersing powders of the products in ethanol, placing a drop of the clear solution on a carboncoated copper grid and subsequent drying. Coin cells of the 2032 configuration were assembled in an argon-filled VAC MO40-1 glove box in which the oxygen and water contents were maintained below 2 ppm. The carbon electrodes for the cells were prepared by blade-coating a slurry of 90 wt.% of the peanut shell carbon, 8 wt.% PVdF and 2 wt.% of carbon black in N-methyl-2-pyrrolidone on a copper foil,

followed by drying at 110 °C in an air oven, roller-pressing the dried sheets, and punching out circular discs. The carbon electrode was coupled with lithium metal in the coin cell, with a 1 M solution of LiPF<sub>6</sub> in a 1:1 (v/v) mixture of EC-DEC. Galvanostatic charge–discharge profiles were recorded between 3.00 and 0.005 V at a 0.1 C rate on a Maccor Series 4000 multi-channel battery tester. The carbons studied are designated in this paper as C-*n*-*x*, where *n* stands for the porogen/peanut shell weight ratio, and *x* for the temperature at which the carbons were synthesized.

# 3. Results and discussion

#### 3.1. Thermal analysis

The TG and DTA curves recorded with the porogentreated and the untreated peanut shell samples between room temperature and 900 °C are shown in Fig. 1. The endotherm and the corresponding weight loss centered around 100 °C in Fig. 1a are due to the loss of superficial moisture from the shells. Between 300 and 400 °C a second endotherm appears. This is accompanied by a major weight loss associated with the destructive distillation of the shells to yield low-volatile organics. In fact, the weight loss continues beyond 400 °C and up to 600 °C, with a third weight loss centered around 420 °C. The physical processes associated with the desorption of moisture from the shells and the chemical processes associated with the subsequent decomposition reactions are necessarily endothermic because the system has to absorb heat from its surroundings to raise its enthalpy to the critical limit of thermodynamic stability, beyond which desorption/decomposition occurs. The decomposition of the high-energy molecules in the peanut kernel into low-energy small molecules should, in principle, be exothermic, a fact reflected by the sudden rise in the DTA curve towards exothermic regions above the 500 °C range. The exotherm is somewhat camouflaged since it is sandwiched between two closely associated endothermic processes: the endothermic absorption of heat before the decomposition reaction and the endothermic processes associated with the sluggish formation and subsequent organization of the carbon layers. The third endotherm is associated with a further loss of volatile vapors and aromatic condensation processes that are part of the intricate pyrolytic reactions. The thermal behavior of the porogen-treated peanut shell (Fig. 1b) differs from that of the untreated one in that there is an extra endothermic event taking place around 235 °C, which may be associated with the thermal events occurring in the porogen. There is also a decomposition of the porogenic material accompanying the decomposition and subsequent carbonization of the peanut shell, to the extent that the thermal changes between about 300 and 600 °C merge into one major endothermic domain.



Fig. 1. TG and DTA curves of the treated and untreated peanut shells in argon.

#### 3.2. Composition and structure

Having determined the decomposition-carbonization range, it was decided to study the effect of pyrolysis temperature on the composition of the carbons obtained from the untreated and porogen-treated peanut shells at a fixed heating rate of 5 °C/min. The results are presented in Table 1. The unaccounted part of the composition is attributed to oxygen and non-volatile inorganics. According to Boehm [26], oxygen in disordered carbons exists in the form of oxygen-bearing functional groups, such as carboxyls, carboxyl anhydrides, phenols, carbonyls, lactones, quinones, quinone-like structures, etc. It can be seen from the elemental compositions listed in Table 1 that in the case of carbons derived from the untreated shells, the amount of hydrogen with respect to carbon steadily declines as the temperature is raised from 500 to 800 °C. A similar trend is evident in the case of the porogen-treated shells too. However, the H/C ratios are smaller than those of products derived from the untreated shells. The variations in the elemental compositions between these two carbons are rather difficult to explain, but it is likely that the heat generated during the decomposition of the porogen or any chemical reaction of the products of this decomposition with the shells could have altered the composition of the final product. Table 1 also shows that varying the porogen/ peanut shell ratio did not have any significant effect on the elemental compositions of the carbonaceous products.

Table 1 Compositions of carbons obtained by pyrolysis of treated and untreated peanut shells as a function of temperature

| Sample  | Percentage composition |      |      |      |  |  |  |
|---------|------------------------|------|------|------|--|--|--|
|         | С                      | Н    | Ν    | H/C  |  |  |  |
| C-0-500 | 73.36                  | 3.80 | 1.78 | 0.62 |  |  |  |
| C-0-600 | 79.60                  | 3.15 | 1.71 | 0.47 |  |  |  |
| C-0-700 | 81.21                  | 2.50 | 1.73 | 0.37 |  |  |  |
| C-0-800 | 81.92                  | 1.95 | 1.80 | 0.29 |  |  |  |
| C-5-500 | 84.71                  | 2.80 | 1.97 | 0.39 |  |  |  |
| C-5-600 | 83.62                  | 2.46 | 1.96 | 0.35 |  |  |  |
| C-5-700 | 84.19                  | 2.13 | 2.06 | 0.30 |  |  |  |
| C-5-800 | 85.27                  | 1.93 | 2.15 | 0.27 |  |  |  |
| C-1-500 | 85.01                  | 2.54 | 2.00 | 0.36 |  |  |  |
| C-2-500 | 84.67                  | 2.48 | 2.03 | 0.35 |  |  |  |
| C-3-500 | 84.89                  | 2.82 | 1.88 | 0.40 |  |  |  |
| C-4-500 | 84.13                  | 2.91 | 1.98 | 0.42 |  |  |  |

Heating rate: 5 °C/min; hold time: 1 h.

However, the porogen treatment tremendously altered the surface structure. For example, the surface areas of C-0-600 and C-5-600 samples were 31.6 and 2098.9 m<sup>2</sup>/g, respectively. The corresponding average pore sizes were 17.6 and 33.6 Å. Treatment with the porogen is found to have effected a 66-fold increase in the surface area, with an attendant opening up of the pores by a factor of almost two. The rate of heating also had little effect on the final composition of the disordered carbons. Table 2 shows that the H/C ratios are nearly constant even after a 10-fold increase in the heating ramp from 0.5 to 5 °C/min. All the subsequent pyrolysis operations were, therefore, done at a heating rate of 5 °C/min.

The TEM images of the carbonaceous materials obtained by pyrolysis at 600 °C at a heating rate of 5 °C/min are shown in Fig. 2 for the products obtained without porogen and with a porogen/peanut shell ratio of 5. Fig. 2a shows that the product obtained without the porogen has the carbon material dispersed in a finely divided state with no discernible ordering. However, the product obtained from the porogen-treated peanut shell possesses some extremely fine fibrous material spread in a shapeless contour (Fig. 2b). Some nanovoids can also be noticed.

Powder X-ray diffractograms of the products obtained by pyrolysis of the untreated shells at different temperatures

Table 2

Effect of heating rate on the elemental composition of carbons derived from untreated peanut shells

| Element | Weight percent |            |            |            |  |  |
|---------|----------------|------------|------------|------------|--|--|
|         | 5.0 °C/min     | 2.5 °C/min | 1.0 °C/min | 0.5 °C/min |  |  |
| N       | 1.71           | 1.88       | 1.82       | 1.88       |  |  |
| С       | 79.60          | 80.90      | 80.02      | 79.36      |  |  |
| Н       | 3.15           | 3.14       | 3.05       | 3.23       |  |  |
| H/C     | 0.47           | 0.47       | 0.46       | 0.49       |  |  |

Pyrolysis temperature: 600 °C; hold time: 1 h.

(a) <u>20nm</u>

Fig. 2. TEM images of pyrolytic products obtained (a) without porogen; (b) with a porogen/peanut shell ratio of 5. Pyrolysis conditions: 600 °C, 5 °C/min, 1 h.

20nm

(hold time: 1 h; heating rate: 5 °C/min) are presented in Fig. 3a. The XRD patterns represent those of highly disordered carbons. Peaks that evolved with an increase in temperature are noticeable, with the characteristic  $(0\ 0\ 2)$ and (100) peaks discernible at 800 °C. In other words, graphite-like domains begin to evolve as the temperature is raised. The  $(1\ 0\ 0)$  reflections around  $43^{\circ}$  indicate the presence of honeycomb structures formed by  $sp^2$  hybridized carbons. The broad (0 0 2) reflections between 20 and  $30^{\circ}$ indicate small domains of coherent and parallel stacking of the graphene sheets. It can also be noted that the  $d_{002}$  values for the C-0-600 and C-0-700 carbons (3.86 and 3.75 Å, respectively) are substantially higher than that for graphite (3.345 Å). According to Liu et al. [8] the quantity of single layers in carbon materials prepared by low temperature pyrolysis may be estimated from the empirical R factor. Rfactor values of <2 for all the samples indicate large concentrations of non-parallel single layers of carbon. However, the increase in R factor as the temperature was raised



Fig. 3. (a) Powder X-ray diffractograms of (top) products obtained by the pyrolysis of untreated shells at different temperatures (hold time: 1 h; heating rate:  $5 \degree C/min$ ); (bottom) C-0-600 carbons obtained at different heating ramps.

indicates that at higher temperatures the single layers become mobile resulting in their parallel orientation with respect to one another. Thus, as more single carbon layers align themselves into small domains of ordered structures, the carbon tends to be increasingly graphitic in nature. These structural characteristics have direct implications on the electrochemical performance of the carbon as lithium-intercalating anodes.

The X-ray diffraction patterns of C-0-600 carbons obtained at different heating ramps are shown in Fig. 3b. Although the temperature was only 600 °C, the longer duration of heating at lower heating rates could have led to more structured domains. The progressive evolution of the (0 0 2) and (1 0 0) peaks and the gradual increase in the *R* factor suggest a build-up of structured domains. It can also be seen that the  $d_{002}$  values increase with an increase in *R* factor values. Such  $d_{002}$  values, being the averages of a multitude of layer spacings, can be somewhat misleading because in turbostratically disordered carbon structures the spacings between the exterior non-parallel layer pairs can be

much larger than the spacings between the interior parallel layer pairs.

Fig. 4a shows the X-ray diffraction patterns of the carbons obtained by pyrolyzing peanut shells treated with different porogen/peanut shell ratios. The pyrolysis temperature was 600 °C and the heating ramp was 5 °C/min. All the diffraction patterns gave broad peaks for the (002) reflections, which became more pronounced as the porogen content increased. While the average  $d_{002}$  values decreased with the amount of porogen, there was a more or less general increase in the value of R factor as the porogen amount was increased. Porogens are not normally expected to alter the crystallographic parameters of the products. However, the increased d<sub>002</sub> values observed for carbons derived from porogen-treated shells must be attributed to the turbostratic disorder due to extensive buckling of carbon layers (as a result of the evolution of gaseous decomposition products from the porogen) leading to an increase in the average values for the d<sub>002</sub> spacings. While a weak broad peak corresponding to the (100) reflections can be seen for



Fig. 4. (a) Powder X-ray diffraction patterns of carbons obtained (top) by pyrolyzing peanut shells treated at different porogen/peanut shell ratios (pyrolysis temperature: 600 °C); (bottom) from porogen-treated shells (porogen/peanut shell ratio: 5) heated to different temperatures. Heating rate and hold time for all the samples: 5 °C/min and 1 h.

the C-5-600 sample, similar peaks are not discernible for the other samples.

Fig. 4b presents the powder X-ray diffraction patterns of carbons derived from porogen-treated shells (porogen/peanut shell ratio = 5; heating rate: 5 °C/min; and hold time: 1 h) at different temperatures. Again, a distinctive evolution of the (0 0 2) and (1 0 0) reflections can be noted with increasing temperature. Curiously, all the samples, including the one heated at 500 °C, showed high values (>2) for the *R* factor, suggesting a slightly higher degree of organized layers than the corresponding carbons obtained from untreated shells.

#### 3.3. Galvanostatic charge-discharge studies

The C-0-500 carbon was not considered for further studies because it was found to be inactive. The inactivity of this carbon is due to (i) the temperature being insufficient for the carbonization–aromatization processes to commence, 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.

All the carbon samples used for electrochemical studies in this work were prepared at 600 °C at a heating ramp of 5 °C/ min, unless otherwise specified. The galvanostatic charge– discharge curves recorded with carbons derived from the untreated peanut shells are shown in Fig. 5a–c. The first lithium insertion capacities (charging of the carbons) were 729 mAh/g for C-0-600, reduced to 613 mAh/g for C-0-700 and further to 402 mAh/g for C-0-800. For the C-0-600 sample, the first-cycle lithium intake was 729 mAh/g, with only 336 mAh/g equivalent of lithium retrievable. This corresponds to an irreversible capacity of 393 mAh/g, or 54% of the input. However, in the subsequent cycles the coulombic efficiencies were 94% or above, reaching 100%



Fig. 5. Charge–discharge curves of carbons derived from untreated peanut shells (voltage range: 3.00–0.005 V; rate: 0.1 C): (a) C-0-600; (b) C-0-700; and (c) C-0-800.

in the fifth-cycle, with charge–discharge capacities of 313–312 mAh/g. For the C-0-700 and C-0-800 samples, the first-cycle irreversible capacities were 50 and 52%, respectively. Although fifth-cycle coulombic efficiencies were 100 and 98%, respectively, their lithium intakes were only 272 and 197 mAh/g.

The high first insertion capacities and irreversible capacities are attributed to the high H/C ratios of these lowtemperature pyrolytic carbons [27,28] as well as to the presence of a large number of nanopores [23-25,29]. According to Dahn et al. [27,28] hydrogen-containing carbons show capacities proportional to their hydrogen content, and exhibit large hysteresis. These authors [27,28] also suggest that such low-temperature carbons have an abundance of nanopores. It can be seen from Table 1 that the H/C ratio (0.47) is the highest for the carbon prepared at 600  $^{\circ}$ C. This ratio decreases to 0.37 and 0.29, respectively, as the temperatures are raised to 700 and 800 °C. The lower resolution of the characteristic (0 0 2) reflections coupled with the small value of the R factor (1.62) suggest that the carbon synthesized at 600 °C has 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. According to Dahn's 'falling cards model' [30], at the low temperatures at which these carbons are formed, there is insufficient thermal energy for the graphene sheets to rotate into a parallel alignment. Thus, the low-temperature carbons have a larger number of non-parallel, unorganized single layers of carbon, giving rise to a low value for the R factor. The presence of such uncorrelated graphene fragments plays an important role in the amount of lithium that a carbon sample can insert [4], but 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, the carbon sample prepared at 600 °C should have unorganized single layers of carbon and nanopores, which should result in high lithium storage capacities. As the formation temperatures of the carbons are raised to 700 and 800 °C, the diminishing of the unorganized domains and the attendant enlargement of the average pore size should lessen the amount of lithium intake into the carbon matrix.

Furthermore, the increase in the formation temperature leads to a decrease in the H/C ratio, which has been shown to be an index of the 'excess' lithium intake by low-temperature pyrolyzed carbons [4,27,28]. The hydrogen is believed to 'saturate' the dangling bonds on the edge carbons of graphene fragments, forming polyaromatic hydrocarbons [9]. Papanek et al. [9] have shown by ab initio calculations that the energy required for lithium intercalation and for lithium to bind to these hydrogen-saturated sites are not very different. Thus, lithium intercalation and lithium binding to hydrogen-saturated carbons must occur at similar potentials, contributing to the excess lithium capacity. The high irreversible capacities of these carbons are apparent from their charge-discharge profiles. Dahn et al. [27,28] attribute the large hysteresis in hydrogen-containing carbons to the (H-C)-Li bridging, in which a two-coordinated edge carbon with a hydrogen would transform from the  $sp^2$  to the  $sp^3$  hybridized form. Mabuchi et al. [23–25] suggest that the 'excess' lithium capacity is due to lithium occupying sites inside the nanopores that are present between the large number of unorganized carbon sheets, from which it is often difficult to retrieve the lithium. The irretrievability of inserted lithium is a major contributor to irreversible capacity in disordered carbons. It is also possible that the large surface areas of these carbons provide ample sites for passivation and consequent loss of capacity. The nanovoids (Fig. 2) facilitate insertion of large amounts of lithium, part of which subsequently is lost due to extensive passivation. The products of passivation progressively accumulate on the carbon surface, clogging the small pores and cavities that would otherwise have been available for the reversible lithium insertion reaction. Thus, the progressive elimination of sites for lithium insertion leads to a progressive drop in the insertion capacity as the cycling proceeds.

The effect of the heating rate on the charge-discharge behavior of the carbons is presented in Fig. 6. With the pyrolysis temperature fixed at 600 °C, the rates of heating were varied (0.5, 1.0, 2.5 and 5.0 °C/min). It can be seen that at the lowest rate of heating (0.5 °C/min), the first lithium intake capacity was 859 mAh/g. It fell to 836, 789, and 729 mAh/g at 1.0, 2.5 and 5.0 °C/min, respectively. Similarly, the irreversible capacities also tended to decrease as the heating rate was increased. In the first five cycles, the capacity fade also decreased as the heating rate was increased. These capacities cannot be related to the hydrogen content in these carbons as the H/C ratios do not seem to vary with the rate of heating (Table 2). When the heating rate is high, the evolution of gases from the organic matter becomes vigorous, creating voids of large and varied sizes. However, a longer duration of heating at low heating rates results in a slow and sustained evolution of volatile organics. Consequently, the sustained low-rate evolution of gases can develop a large number of nearly uniform-sized nanopores in the carbon matrix [31]. Simultaneously, the longer heating duration can lead to a slow alignment of the unorganized single carbon sheets. The increased number of nanopores should contribute to increased lithium insertion capacities, while the increased alignment of the single carbon planes should reduce the double surfaces available for lithium occupancy. Two processes, one aiding greater lithium capacity, and the other reducing the sites available for lithium insertion, run in parallel. The net result of these opposing processes decides the first discharge capacity of the carbon. The importance of thermal processing conditions for the synthesis of carbonaceous materials with structural



Fig. 6. Effect of heating rate on the charge-discharge behavior of C-0-600.

characteristics suitable for optimum electrochemical performance is thus clear.

The insertion capacities of the carbons derived at 500 °C from porogen-treated shells with different porogen/peanut shell ratios are shown in Fig. 7. The fact that the carbons derived by heating porogen-treated shells gave good capacities while those derived from the untreated shells did not, goes to show that the heat generated during the exothermic decomposition of the porogen resulted in the carbonization and aromatization of the carbon-containing material even though the treatment temperature was only 500 °C. The firstcycle lithium intake by the carbons derived from porogentreated shells recorded an exponential increase from 423 mAh/g for the C-1-500 sample to 1809, 3670, 4010 and 4765 mAh/g, respectively, when the porogen/peanut shell weight ratio was raised to 2, 3, 4 and 5. The corresponding values in the second cycle were 54, 240, 1242, 1595 and 1522 mAh/g. At the tenth cycle the insertion capacities were 41, 24, 966, 1366 and 1427 mAh/g. The irreversible capacities recorded in the first cycle for the carbons were 395, 1390, 2559, 2908 and 2380 mAh/g at the respective porogen/peanut shell ratios. The inordinately high values of the capacities recorded may be compared to the theoretical value of 3862 mAh/g that is possible with lithium metal. Such high values for lithium accommodation suggest that the packing densities of the inserted lithium in these structures are much higher than in the metal itself, if all the lithium is indeed inserted. In such a case, the local environment of lithium in these carbons must be quite different from that obtained with the LiC<sub>6</sub> compositions in highly graphitized structures. Structural investigations of such lithiated carbons obtained from porogen-treated peanut shells should be of much interest. The simultaneous possibilities of lithium interacting with surface functional groups on the carbons, and plating on carbon surfaces followed by passivation upon reaction with the electrolyte are not ruled out.



Fig. 7. Effect of porogen/peanut shell ratio on the lithium insertion capacities of the carbons derived at 500  $^\circ$ C.

| Table 3                                  |          |          |       |        |
|--|----------|----------|-------|--------|
| Lithium insertion capacities of C-5-500, | C-5-600, | C-5-700, | and C | -5-800 |

| Cycle<br>number | 500 °C | 500 °C |      | 600 °C |      | 700 °C |      | 800 °C |  |
|-----------------|--------|--------|------|--------|------|--------|------|--------|--|
|                 | IC     | DC     | IC   | DC     | IC   | DC     | IC   | DC     |  |
| 1               | 4765   | 1385   | 3504 | 1650   | 2783 | 1509   | 2977 | 1415   |  |
| 2               | 1522   | 1285   | 1744 | 1566   | 1649 | 1540   | 1561 | 1433   |  |
| 3               | 1485   | 1304   | 1668 | 1551   | 1655 | 1567   | 1519 | 1439   |  |
| 4               | 1444   | 1314   | 1646 | 1559   | 1627 | 1539   | 1515 | 1439   |  |
| 5               | 1429   | 1315   | 1638 | 1552   | 1616 | 1536   | 1508 | 1431   |  |
| 6               | 1401   | 1318   | 1635 | 1554   | 1608 | 1548   | 1493 | 1420   |  |
| 7               | 1413   | 1332   | 1616 | 1538   | 1604 | 1517   | 1565 | 1464   |  |
| 8               | 1411   | 1341   | 1632 | 1549   | 1578 | 1500   | 1470 | 1395   |  |
| 9               | 1418   | 1353   | 1627 | 1543   | 1563 | 1483   | 1443 | 1362   |  |
| 10              | 1427   | 1363   | 1579 | 1504   | 1485 | 1389   | 1419 | 1348   |  |

Charge-discharge rate: 0.1 C; range: 3.0–0.005 V. IC: insertion capacity; DC: deinsertion capacity.

In fact, the high activity of such surfaces may permit lithium plating at potentials more positive than the lithium equilibrium potential. Nevertheless, the high values for the deinsertion capacities call for a deeper understanding of the lithium insertion processes in these carbons. The partial buckling and exfoliation of the carbon matrix by the slow and sustained evolution of gases from the porogen during the carbonization process can lead to structures with large surface areas and pore volumes, as well as an augmentation in the number of double surfaces which may roll into nanopores. The excess lithium may locate on the zigzag and arm-chair faces of the individual layers [32,33] and in such nanoscopic cavities [23–25,29,34].

Table 3 lists the lithium insertion capacities of C-5-500, C-5-600, C-5-700, and C-5-800 at a charge–discharge rate of 0.1 C in the 3.0–0.005 V region. It can be noted that the first lithium intake capacity decreased from a high of 4765 mAh/ g for the sample synthesized at 500 °C to 2977 mAh/g as the pyrolysis temperature was raised to 800 °C. The degree of irreversibility gradually decreased in the subsequent cycles for all the samples. However, the C-5-600 sample maintained consistently high values for the lithium deinsertion capacity in all the subsequent cycles. The high irreversible capacities and the continued loss of capacity with cycling will remain a question mark over the applicability of these carbons in practical cells unless measures are devised to eliminate or lessen these irreversible losses.

## 4. Conclusions

Disordered pyrolytic carbons prepared from peanut shells in argon have been shown to possess high capacities for lithium intake. The treatment of the shells with a porogenic agent results in carbon materials with a 66-fold increase in surface area, and initial lithium intake capacities of as much as 4765 mAh/g. The high capacities in these disordered carbons are believed to be due to the binding of lithium on the extra surfaces of the single layers of carbon and the accommodation of extra lithium in the nanoscopic cavities formed in the carbon matrix by the diffusion of gaseous decomposition products of the porogen through the carbon. Part of the 'excess' capacity may also be attributed to the interaction of lithium with the surface functional groups on the carbon as well as to lithium plating on the carbon surface and subsequent passivaton upon reaction with the electrolyte. Despite the abnormally high initial capacities exhibited by these carbons, their high irreversible capacities and continued loss in capacity with cycling prevent their applicability in high-energy lithium-ion batteries.

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