

Spherical natural graphite coated by a thick layer of carbonaceous mesophase for use as an anode material in lithium ion batteries

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Abstract A method for coating a thick layer of carbonaceous mesophase was developed to treat spherical natural graphite (SNG) for use as anodes in lithium ion batteries. The carbonaceous mesophase layer was fabricated by heat treatment of a mixture of SNG and coal tar pitch. The thickness of the carbonaceous mesophase on the surface of the SNG was approximately 2.5 μm , which is effective for enhancing the strength of the carbonaceous mesophase shell and for allowing the shell to maintain good integrity at a high anode density (1.6 g cm^{-3}). The mesophase layer increased the initial coulombic efficiency from approximately 90% to 95%, dramatically improved the capacity retention and reduced the irreversible capacity by greatly decreasing the SNG surface area. The initial efficiency, cycle life and rate capability for the SNG anode covered by a thick mesophase layer gave comparable results as the mesocarbon microbeads (MCMB) anode, while the SNG anode reversible capacity of 341 mAh g^{-1} was higher than that of MCMB, 319 mAh g^{-1} . Electrochemical measurements showed that SNG particles coated by a thick carbonaceous mesophase layer are strong

candidates for use as possible anode materials in high energy density lithium ion batteries.

Keywords Spherical natural graphite · Carbonaceous mesophase · Lithium ion battery · Anodes

1 Introduction

Since Sony introduced a carbon material instead of lithium metal as a negative electrode and obtained the first commercial lithium ion cell, many carbon materials, such as natural graphite, cokes and graphitized carbons, have been widely investigated as alternative anodes in rechargeable lithium ion batteries. Of all the various carbon materials, natural graphite appears to be the most desirable candidate due to its high specific capacity, low cost and desirable charge potential profile [1–4]. In practical applications, however, irreversible reactions that take place between the lithium and the electrolyte during the first cycle and poor cycle life have been persistent problems that limit the wide scale application of natural graphite anodes. This is due to the fact that natural graphite is a layered material with an anisotropic surface structure and weak bonds (Van der Waals forces) between the graphene layers [2–6]. These structural characteristics enable natural graphite to be easily exfoliated, which results in a breakdown of the SEI film formed on the external surface of natural graphite; therefore, the formation of a new SEI film unavoidably occurs on the surface freshly exposed to electrolytes. This is the reason why a natural graphite anode often has a large irreversible capacity and a limited cycle life. On the other hand, the irreversible capacity associated with graphite depends considerably on the electrolytes and especially on the solvents used. For example, irreversible reactions are

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worse in propylene carbonate (PC)-based electrolytes than those found in ethylene carbonate (EC)-based electrolytes [7–9]. This means graphite has a limited compatibility with different electrolytes.

In order to overcome the disadvantages of natural graphite anodes, vigorous investigations using possible surface modifications have begun. Many species, such as coke and metals, have been introduced onto the graphite surface to suppress the irreversible solvated lithium intercalation into graphite [7, 10–12]. Of all the various surface modifications, coating the natural graphite by additional carbons was considered to be the most effective method to improve the reversible capacity and cycle life of natural graphite electrodes in lithium ion batteries [4, 13–19]. When a natural graphite surface is coated by a carbon “shell”, a smaller surface area can usually be obtained, which may decrease the irreversible capacity during the first cycle and improve the compatibility of the graphite anode with the electrolyte [13]. In fabrication of lithium ion batteries, the anodes often need to be pressed to obtain a high volumetric energy. However, the high pressures in the rolling and pressing processes may destroy the coated carbon shell and expose the graphite surface once again to the electrolytes if the carbon “shell” is very thin and not sufficiently strong [9]. This fragility of the thin shell hinders its practical application. In this work, we used mesophase-pitch carbon to coat natural graphite and to obtain a thick “shell” that had good flexibility and maintained its integrity under high pressure. This material has the potential to be commercialized for use as anodes in lithium ion batteries.

2 Experimental

Preparation of the carbonaceous mesophase-coated SNG particles was conducted as follows. Spherical natural graphite (SNG) particles were initially dispersed in coal tar pitch. This was followed by liquid carbonization, which was carried out by heating the system up to 410 °C for 4 h under continuous stirring, after which the system was allowed to cool naturally back to room temperature. The carbonaceous mesophase material generated from the heat-treated pitch covered the surface of the SNG particles.

The mesophase-coated SNG particles were dissolved and isolated with the organic solvent toluene, and dried by evaporating away the solvent under 60 °C for 15 h. Finally, the mesophase-coated particles were carbonized by heat treatment at 1,000 °C for 1 h under the protection of high-purified nitrogen and then graphitized at 2,800 °C without holding under the protection of purified argon.

For comparison, pure mesocarbon microbead (MCMB) particles were obtained by using the same coal tar pitch as starting material and by using a liquid carbonisation time of 10 h. Table 1 lists some of the properties of the naked SNGs, the carbonaceous mesophase-coated SNGs and the MCMBs.

The average size of the carbon particles in the powder was measured using a Malvern laser diffraction analyzer (MS 2000), and the surface areas of the carbon particles were determined by nitrogen adsorption using the BET method with a Micromeritics ASAP 2020. Scanning electron microscopy (FEI Quanta 200) and the cross-polarized imaging method (ZEISS Axioplan 2 Imaging, German) were employed to investigate the surface morphology of the graphite samples.

For testing the electrochemical properties, a carbon electrode was prepared from a slurry comprising 95% graphite materials, 1% carbon black (Super-P) and 5% binder (a mixture of carboxymethyl cellulose sodium (CMC) and styrene butadiene rubber (SBR)). The slurry was mixed homogeneously in an electric mixer and the resulting slurry was roller coated onto a copper foil current collector and dried under vacuum at 120 °C for 12 h. The resulting pellet was pressed and cut to a suitable size for the different electrochemical measurements.

The first charge–discharge behavior of each sample was carried out on coin cells using an Arbin Battery Test (BT-2043) at a rate of C/10 with cutoff potentials of 0.005 V and 1.0 V versus Li/Li⁺. A metallic Li sheet was used as the counter electrode. Tests of the cycle life and rate capability of the test electrodes were carried out on 063048 prismatic batteries, where a LiCoO₂ positive electrode was used as a counter electrode with cutoff potentials of 3.0 V and 4.2 V. For all the test cells, Celgard 2400 was used as a separator and a solution consisting of 1 M LiPF₆ in a 1:1:1 mixture of EC/DEC/DMC was used as an electrolyte. All the test cells were assembled in a glovebox filled with

Table 1 Properties of the SNGs, the carbonaceous mesophase-coated SNGs and the MCMBs

| | Particle size (μm) | Specific surface area (m ² g ⁻¹) | Reversible capacity (mAh g ⁻¹) | Efficiency (%) |
|----------------------|--------------------|---|--|----------------|
| SNG | 15.92 | 3.6 | 362 | 90.3 |
| Mesophase-coated SNG | 20.59 | 1.7 | 341 | 95.0 |
| MCMB | 17.23 | 1.4 | 319 | 94.6 |

argon gas and all experiments were performed at room temperature.

3 Results and discussions

3.1 Characterization of carbonaceous mesophase-coated SNGs

The cross-polarization images of the bare SNGs and the carbonaceous mesophase-coated SNGs are shown in Fig. 1a and b, respectively. From Fig. 1 it can be seen that mesophase-coated SNG particles are larger and more spherical than the bare SNGs. According to the colour differences of the different sections in cross-polarization images, a “core-shell” structure of the coated SNG can be clearly seen in Fig. 1b. The cores were SNG particles. The outside of the SNG particles are carbonaceous mesophase, which makes the SNG particles more spherical and smoother. These results indicated that the carbonaceous mesophase is generated on the surface of the SNG particles in the coal tar pitch. The mean thickness of the coating layer can be estimated as one-half the difference of the mean diameters of the carbonaceous mesophase-coated SNG (D_1) and the bare SNG (D_0), i.e., $(D_1 - D_0)/2$. The mean diameters of the carbonaceous mesophase-coated SNG and naked SNG particles, which were determined using a Malvern laser diffraction analyzer, were found to be 20.59 μm and 15.92 μm , respectively (Table 1); this gives an average coating layer thickness of 2.335 μm , which should be large enough to provide some distinguishing features to the carbonaceous mesophase-coated SNG particles, e.g., pressure resistance.

Figure 2a–c show typical SEM images of the bare SNG, the carbonaceous mesophase-coated SNG and the MCMB particles, respectively. In Fig. 2a, the bare SNG particles are almost potato alike. In Fig. 2b, the carbonaceous mesophase-coated SNGs are more spherically shaped than the SNG particles and are similarly shaped as the MCMB

particles shown in Fig. 2c. The morphology of the carbonaceous mesophase-coated SNGs was smoother than that of the bare SNGs and was very similar to that of the MCMBs. This was due to the fact that the coating layer of carbonaceous mesophase smoothes over the imperfections of the SNG surface. The fabrication of the carbonaceous mesophase layer and the MCMB particles used the same coal tar pitch, which was the reason why the texture of the carbonaceous mesophase-coated SNGs was similar to the MCMBs. As a result of the thick, smooth carbonaceous mesophase coating, the carbonaceous mesophase-coated SNGs had a much lower surface area than the bare SNGs (1.7 $\text{m}^2 \text{g}^{-1}$ compared with 3.6 $\text{m}^2 \text{g}^{-1}$), which is beneficial in regards to the first reversible capacity.

In order to estimate the effect of the thick mesophase shell in practical batteries, for comparison, the SNG particles coated by a thin layer of carbonaceous mesophase were obtained by using a liquid carbonization time of 1.5 h. Its average coating layer thickness, calculated from the data of the mean diameter determined by a Malvern laser diffraction analyzer, is ca. 400 nm. This value is much lower than that of particles liquid carbonized for 4 h. The anodes made by these two types of mesophase-coated SNG particles were both pressed to get a density of 1.6 g cm^{-3} . The pressures applied to the thin coating layer and the thick coating layer were 2.5 tonne cm^{-2} and 4 tonne cm^{-2} , respectively. The SEM images of the pressed anodes are shown in Fig. 3. It can be clearly seen that the particles coated by a thin layer were split in pressing due to the deformation of parent SNG particles, while the particles coated by a thick layer kept its integrity. It is expected that the splitting of the coating layer will expose the surface of SNG particles once again to the electrolytes and inevitably reduce the electrochemical performance. Hence, in order to keep its integrity, the shell should have enough strength to resist the deformation of SNG particles under high pressure. When the mesophase coating layer is thick the strength of the shell increases. As a result deformation of the mesophase-coated SNG particles under

Fig. 1 Cross-polarization images of (a) the naked SNGs and (b) the carbonaceous mesophase-coated SNGs

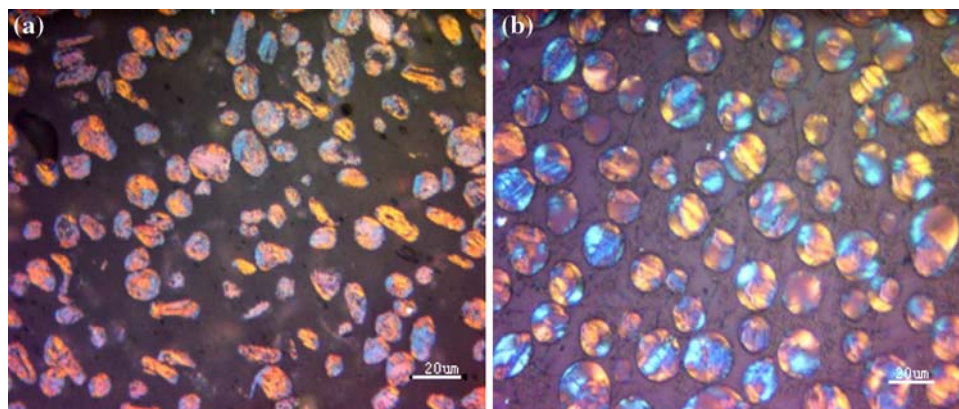


Fig. 2 Typical SEM images of (a) the bare SNG, (b) the carbonaceous mesophase-coated SNG and (c) the MCMB particles

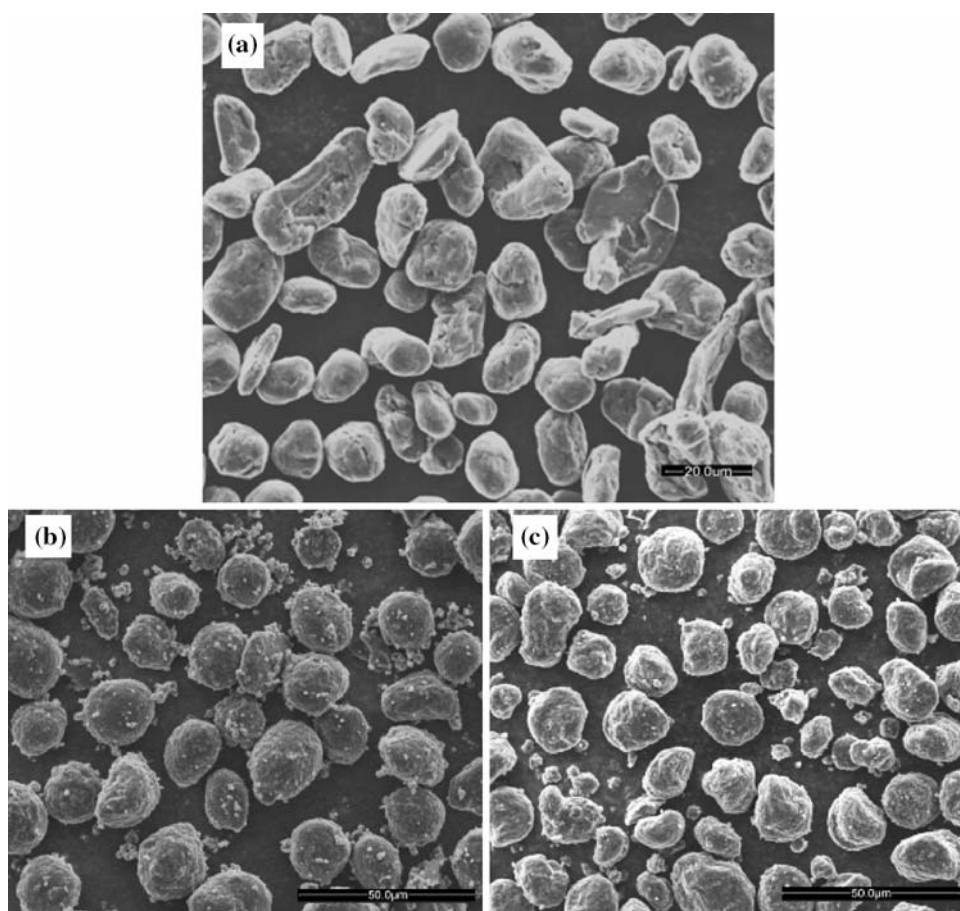
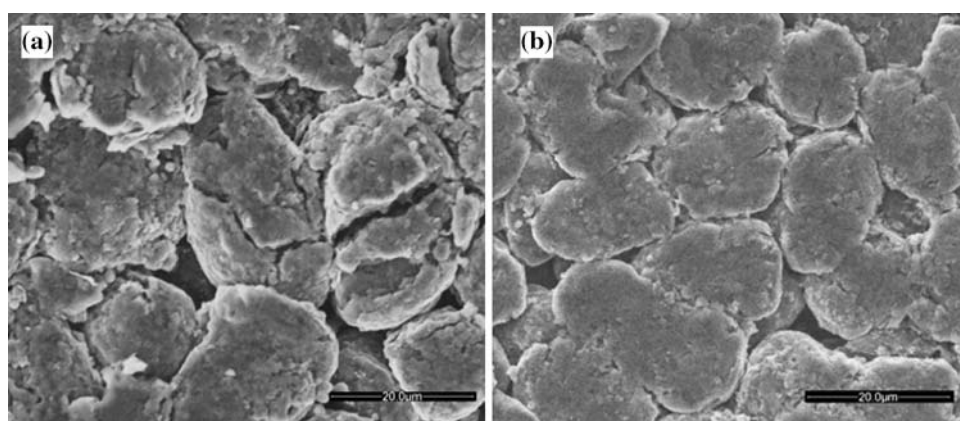


Fig. 3 Typical SEM images of the pressed anodes made by particles with (a) a thin coating layer and (b) a thick coating layer



pressure decreases, which is beneficial in protecting the SNG surface from electrolyte.

3.2 Electrochemical properties of the MCMB-coated SNG anodes

In order to estimate the effect of a thick “shell” (i.e., the thick carbonaceous mesophase coating layer) on the electrochemical properties of the carbonaceous mesophase-coated SNGs, all anodes (the bare SNGs, the carbonaceous

mesophase-coated SNGs, and the MCMBs) were roller pressed at high pressure. The densities of the carbonaceous mesophase-coated SNG and SNG anodes were both 1.6 g cm^{-3} , which are practical values for use in commercial lithium ion batteries. For our MCMB anode, owing to its high strength, the density we could apply on the full battery was 1.55 g cm^{-3} , which was the highest value. In order to obtain these high densities, the pressures applied to the bare SNGs, the carbonaceous mesophase-coated SNGs, and the MCMBs were 1.5, 4 and 8 tonne cm^{-2} , respectively.

The initial reversible capacities and efficiencies of the carbonaceous mesophase-coated SNG, the naked SNG and the MCMB anodes, which were obtained from coin cells, are given in Table 1. The initial efficiency of 90% for the SNG anode was much lower than that of carbonaceous mesophase-coated SNG and MCMB anodes (which were both about 95%) and even displayed a high-reversible capacity. It is expected that an even worse cycle life would appear under full battery conditions. Since the Li content is limited by the LiCoO_2 cathode for a full lithium ion battery, the low initial efficiency of the SNG anode suggests that a SNG anode would consume more LiCoO_2 material to form solid electrolyte interphase, thereby resulting in an increase in the overall cell cost and causing other serious safety problems. For the carbonaceous mesophase-coated SNG anodes and the MCMB anodes, a much higher efficiency than that of the SNG anodes was obtained; this can be attributed to the carbonaceous mesophase coating layer. The coating layer decreases the SNG surface area, removes some active sites at the naked SNG surface and hides some structural defects. As a result the irreversible side reactions leading to capacity fading are reduced. The similarity in texture of the carbonaceous mesophase-coated SNG and the MCMB and the integrity of coating layer under pressing condition explains their similar initial coulombic efficiency. There is another valuable result shown in Table 1. The reversible capacity of the carbonaceous mesophase-coated SNG anode, 341 mAh g^{-1} , was lower than that of the naked SNG, 362 mAh g^{-1} ; a similar result has been found using another coating method [10, 11]. The decrease in the total reversible capacity of the carbonaceous mesophase-coated SNG anode is due to the fact that MCMB has a lower reversible capacity than SNG (see Table 1).

Figure 4 shows the initial charge–discharge curves of the bare SNG, the carbonaceous mesophase-coated SNG and the MCMB anodes. For the bare SNG anode, an obvious voltage retention (from about 0.75 to 0.3 V versus Li/Li^+) from the irreversible reaction is clearly visible. However, the voltage retention almost disappears in the charge–discharge curve for the carbonaceous mesophase-coated SNG and the MCMB anodes, which suggests that the coating layer considerably decreases the side reaction from electrolyte decomposition/SEI formation and the high pressure in pressing process does not destroy the coating layer. Carbonaceous mesophase (e.g., MCMB) has been a good commercial anode material in rechargeable lithium ion batteries due to its good texture, good compatibility with electrolytes and good cyclability [19, 20]. The mesophase coating layer on the SNG surface increases SNG compatibility with the electrolyte and its cyclability.

Our study of carbonaceous mesophase-coated SNG was aimed at commercially applying SNGs in lithium ion batteries. In order to investigate the cyclability of the

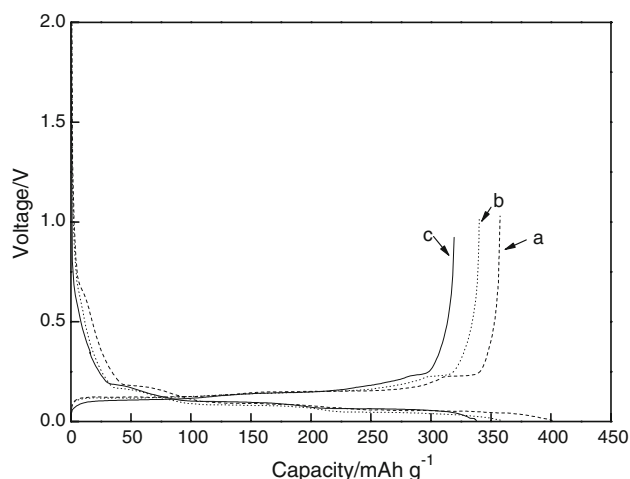


Fig. 4 Initial charge–discharge curves of (a) the naked SNG, (b) the carbonaceous mesophase-coated SNG and (c) the MCMB anodes

carbonaceous mesophase-coated SNG anodes we prepared bare SNG, carbonaceous mesophase-coated SNG and MCMB anodes and tested their cycle life at a 1 C rate on 063048 lithium ion batteries. The anode densities were the same as those used in coin cells and the results are shown in Fig. 5. For the bare SNG material the retention ratio of capacity dramatically decreased upon cycling, where it was found that the battery only held 82% of its initial capacity at its 100th cycle. However, the battery with the carbonaceous mesophase-coated material still kept 90% of its initial capacity even after 300 cycles; a similar result was also observed when the battery used only MCMB as an anode. These results indicate that a thick carbonaceous mesophase coating layer can separate SNG from the electrolyte and be flexible enough to maintain structural integrity under high pressures found during the pressing and rolling stages in the test electrode preparation. According to our results, the

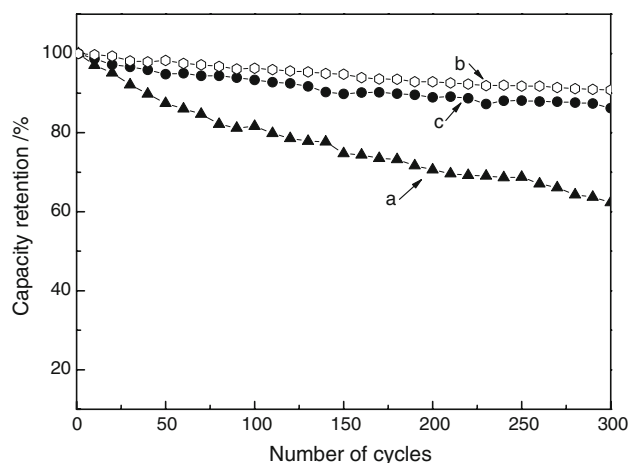


Fig. 5 Capacity retention of the lithium ion batteries at a 1 C rate using (a) the naked SNG, (b) the carbonaceous mesophase-coated SNG and (c) the MCMB anodes

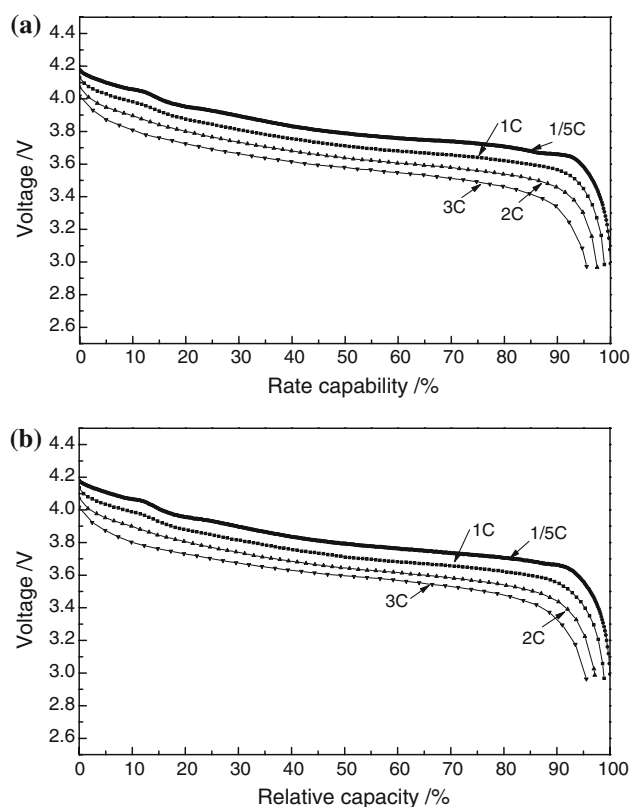


Fig. 6 Relative capacity of lithium ion batteries at different rates using (a) the carbonaceous mesophase-coated SNG and (b) the MCMB anodes

carbonaceous mesophase-coated SNG may be used to replace MCMB in lithium ion batteries in order to improve the energy density.

A comparison of the rate capability of a carbonaceous mesophase-coated SNG anode versus an MCMB anode on a full battery was also investigated. The compositions of the test batteries were the same with the sole exception of the anodes, and the test conditions were also the same. Figure 6a and b show the discharge characteristics of the batteries at different rates using a carbonaceous mesophase-coated SNG anode and a MCMB anode, respectively. The battery using the carbonaceous mesophase-coated SNG anode was able to deliver 98.9% of its C/5 rate capacity at the 1 C rate and 95.5% of its C/5 rate capacity at the 3 C rate. A similar relative capacity was observed for the test battery using the MCMB anode. These results clearly indicate that the carbonaceous mesophase-coated SNGs are promising anode materials for lithium ion batteries.

4 Conclusion

SNG coated by a thick carbonaceous mesophase shell (of the order of a few micrometers) was investigated as an

anode for lithium ion batteries. Coating the SNG with a thick carbonaceous mesophase layer resulted in core-shell structure that was more spherical than the bare SNG. The specific surface area of the SNG decreased greatly after coating with carbonaceous mesophase, which helped to provide high initial columbic efficiency. The initial reversible capacity, initial efficiency, cycle life and rate capability of the carbonaceous mesophase-coated SNGs were investigated and compared with the bare SNGs and the MCMBs. In comparison with bare SNG, our results demonstrated that higher initial columbic efficiency and much better cycle stability can be obtained by coating a thick carbonaceous mesophase layer on the SNGs. The carbonaceous mesophase layer, with a density up to 1.6 g cm^{-3} , was elastic enough to be stable under high pressure during rolling and pressing. Compared with MCMBs, a higher reversible capacity, along with similar initial efficiency, cycle stability and rate capability, was found in the carbonaceous mesophase-coated SNGs, thereby demonstrating their potential as a promising candidate for anodes in high energy density lithium ion batteries.

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