Study of mesophase pitch-based graphite foam used as anodic materials in lithium ion rechargeable batteries

JIE YANG*, ZENG-MIN SHEN, RUI-SHENG XUE
Institute of Carbon Fibers and Composites, Beijing University of Chemical Technology,
Beijing 100029, People's Republic of China
E-mail: yangjie0606@sina.com

ZHI-BIAO HAO
The 43rd Institute of the 4th Academy, China Aerospace Science and Technology Corporation (CASC),
P.O. Box 101, Xi'an, 710025, People's Republic of China

Secondary batteries are one of the possible alternatives, together with supercapacitors and fuel cells, for supplying energy to new electronic devices. Among those, Li-ion batteries are recognized as the most promising because of their lightweight, highly working potential, good cycling behavior, environmental friendly composition, etc. Research and development are in progress to increase the power density and specific capacity of rechargeable lithium ion batteries. Much work focuses on developing advanced carbonaceous materials, which can be used as active anode materials [1–4]. In the past decade, the mesophase pitch carbon has been highlighted in carbon community because of its unique liquid crystal structures. Among the various carbonaceous products from mesophase pitch, the mesocarbon microbeads (MCMBs) and milled mesophase pitch-based carbon fibers (mMPCFs) have been extensively investigated and commercially employed as anode materials [5–9]. It is well known that the performances of lithium ion batteries depend strongly on the microstructures, morphologies and the crystallization degree of meosphase pitch products. Commonly it is difficult to control the MCMBs or mMPCFs to form one certain kind of microstructures. Moreover, the preparation of MCMBs requires complicated separation and expensive purification. As for mMPCFs, fabrication is costly because such process needs special apparatus, also requires the mesophase pitch to have high purity and flowability. However, the carbon foams derived from mesophase pitch [10–13] are novel material with ultra-high thermal conductivity, and they are rich in the highly oriented filament and ligament. As we know, the orientation of carbon dominates its conductivity, which in turn affects the cyclic properties and capacitance of lithium ion batteries to a large extent. In the present work, we attempt to investigate the mesophase pitch carbon foams heat treated at high temperature as anode materials for lithium ion secondary batteries.

The foaming technique used in this study is similar to that reported by Klett *et al.* [10, 11]. The powder of mesophase pitch (softening point: 272 °C) synthesized from FCC decant oil by two steps is poured into a high pressure chamber then heated up to the foaming temperature (500 °C) and maintained for 1 h at the pressure of 2 MPa. Next, the foam samples are carbonized at the rate of 1 °C/min to 1000 °C and then graphitized at the rate of 10 °C/min in argon to 2800 °C with 1 h soak. Finally, the graphite foams are crushed to the size of 1–2 mm and then pulverized to the powder below 240 meshes in the agate mortar with a planetary ball grinder. As shown in Fig. 1a and b, the foams consist of spherical cells, which appear to be open and three-dimensional interconnected. The pore size is distributed in the range of 500–900 μm and the pore walls consist of highly oriented mesophase domains along the axis of the ligament. Moreover, it can be seen that there are many microcracks in the cell walls and junctions. In addition, the textures of powders exhibit the stack of well-orientated planar layers, as shown in Fig. 1c and d. Obviously it is convenient for the lithium ion to access to and impregnate into the inner part of powder through the microcracks and the ragged sections. The aligned graphitic ligament of mesophase pitch-based carbon foams results in a high degree of anisotropy with regard to electrical, thermal, magnetic as well as chemical properties [10–12]. This anisotropy, which is directly related to the preferentially oriented layered structure of graphite, is essential for their application in lithium ion secondary batteries, as the graphitic anode materials do, allowing a large amount of lithium to be inserted [4, 5, 7].

X-ray diffraction (XRD) patterns were recorded with a Rigaku diffractometer (Rad-γ A) using monochromatic Cu K_α (Fig. 2). A sharp diffraction peak appear at $2\theta = 26.32°$, suggesting that graphitized mesophase pitch-based carbon foams have high degree crystallinity and a graphite structure. The average interlayer spacing, d_{002}, the crystallite dimensions L_c (002) and L_a (110) were determined by using Bragg and Scherrer formulas respectively, as shown in Fig. 3. Endo *et al.* reported that well-ordered graphite ($L_{c002} > 20$ nm) and low crystalline materials ($L_{c002} < 3$ nm) have a large capacity [4]. On the basis of these results, it can

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*Author to whom all correspondence should be addressed.

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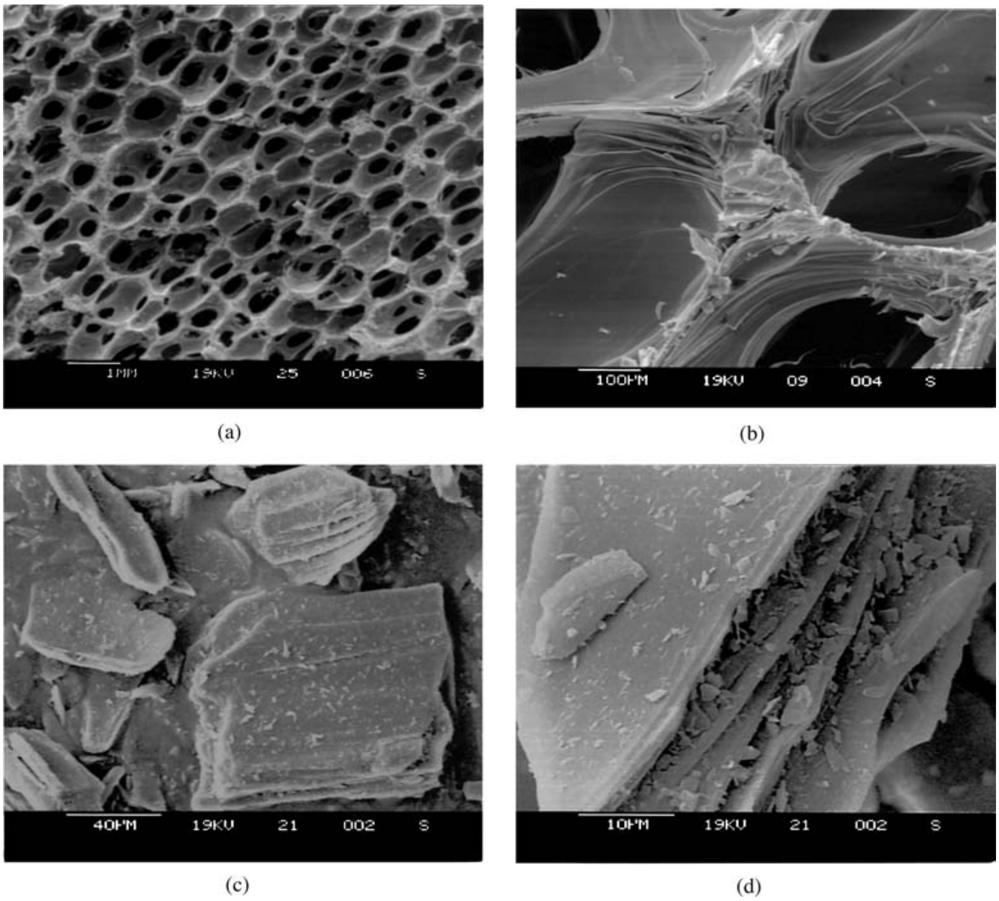

(a) (b)

(c) (d)

Figure 1 Micrographs of mesophase pitch-based graphite foam (a and b) and its powders (c and d), L: Ligament, J: Junction.

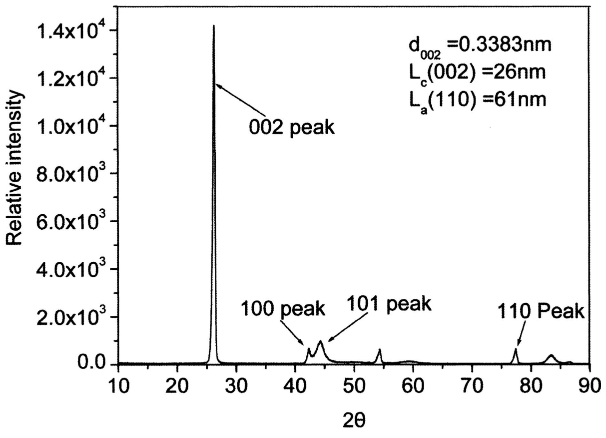

Figure 2 XRD diffraction pattern of mesophase pitch-based graphite foam.

be reasonably inferred that the mesophase pitch-based graphite foams would possess a better electrochemical property.

The electrodes for the sample were prepared by coating slurries of the carbon foams powder (90 wt%), polyvinylidene fluoride (PVDF, 10 wt%) dissolved in N-methyl pyrrolidinone (NMP) on copper foil. The electrode has coverage of 8–12 mg cm^{-2}. Coin-type test cells (CR-2025) were constructed using carbon as working electrodes and lithium foil as counter electrodes. Microporous polypropylene sheet (Celgard) was used as separator. The electrolyte was 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in a 50/50 V/V mixture of ethylene carbonate (EC) and diethyl carbonated (DEC). The cells were assembled in a glove box filled with argon gas, where moisture and oxygen concentration were less than 5 ppm. The cells were charged and discharged with a constant current density of 2 mA cm^{-2} in 0–2.8 V potential ranges.

The charge–discharge curves of the cell are shown in Fig. 3. Theoretically, Li^+ intercalation into carbons is fully reversible and its charge capacity is 372 mAh g^{-1}. For the powder of graphite foams, its charge capacity in the first cycle is 356 mAh g^{-1}, and the discharge capacity of 306 mAh g^{-1} is about 86% of the charge capacity for this cycle. In the second and subsequent cycles, the charge and discharge capacities exhibit no differences and the columbic efficiency is close to 100%. The irreversible specific charge capacity decreased rapidly from about 14% of the first cycle to nearly 0% of the subsequent cycles (Fig. 4). It is note worthy that many world-wide known MCMBs and MPCFs investigated in the same conditions, exhibited a capacity less than 300 mAh g^{-1}. So, the sample shows a good cycleability and a very highly specific capacity. The electrode reaction of sample between 0.8 and 0.2 V involved the irreversible formation of the SEI (solid electrolyte interphase) layer. It can be seen from Fig. 3B that the electrochemical behavior of the graphitized mesophase pitch carbon foam is almost the same as that of other highly graphitized electrodes [13–15], exhibiting one short potential plateau at 0.2 V and two long potential plateaus at 0.1 and 0.07 V. These three potential plateaus correspond to the different Li^+ intercalation

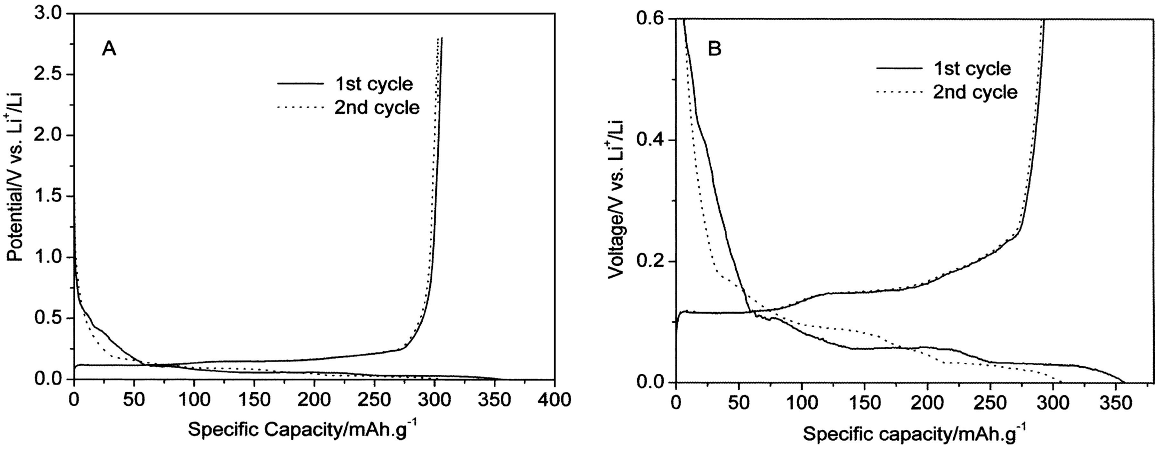

Figure 3 The first and second cycles for the powder from the prepared graphite foam: (A) curves in whole potential region, and (B) magnification of the curves in low potential region.

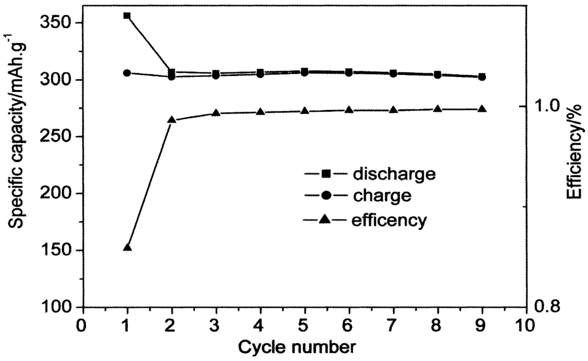

Figure 4 Charge–discharge capacities and coulombic efficiency as a function of cycle number for the sample.

compounds (Li-GICs). On the charge curve, the three potential plateaus occur at 0.1, 0.14, and 0.20 V, corresponding to the Li deintercalation process.

In conclusion, the graphitized mesophase pitch carbon foams exhibit a superior anode performance, which stable capacitance can reach as high as 306 mAh g^{-1} and significantly larger than many highly grapitized anode materials such as MCMBs and mMPCFs. Apparently, this can be considered as a contribution of the orientation of liquid crystal mesophase domains during foaming process. Compared to that of MCMBs and mMFCFs, the preparation of mesophase pitch carbon foam is an inexpensive and simple to obtain high performance carbonaceous material, which would make it a promising anode material for lithium secondary batteries.

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