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High-capacity lithium-ion cells using graphitized mesophase-pitch-based carbon fiber anodes

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Abstract

We have developed high-capacity lithium-ion cells using graphitized mesophase-pitch-based carbon fiber (MCF) as an anode material. The graphitized MCF is a highly graphitized carbon fiber with a radial-like texture in the cross section. This structure contributes to the rapid diffusion of lithium ions inside the carbon fiber. The diffusion coefficient of lithium ions in the graphitized MCF was one order of magnitude larger than those for graphite, resulting in an excellent high-rate performance of the carbon electrode. The graphitized MCF anode showed larger capacity, a higher rate capability, and better reversibility than the graphite anode. The 863448 size (8.6 mm × 34 mm × 48 mm) prismatic cell with the graphitized MCF anode exhibited a large capacity of >1000 mAh. At 3 A discharge, the prismatic cell had 95% of its capacity at 0.5 A discharge with a mid-discharge voltage of 3.35 V. The cell maintained $>85\%$ of its initial capacity after 500 cycles and showed high capacity at -20 °C. It has thus been demonstrated that the prismatic cell using the graphitized MCF anode has excellent performance, and is an attractive choice for the power sources of cellular phones and other appliances.

Keywords: Lithium-ion batteries; Carbon; Carbon fibers; Rechargeable batteries

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1. Introduction

Lithium-ion cells are now considered to be the most promising cells for many portable appliances. Rechargeable C/LiCoO$_2$ lithium-ion cells have been commercialized for use in portable handy phones, personal computers and portable audio-visual equipment. As the application of lithium-ion cells has grown, so has also the demand for longer cell life. Various types of carbon, e.g., graphite, carbon fibers, thermal decomposition products of polymers, pyrolytic carbons and petroleum coke have been proposed as the negative electrodes; their electrochemical characteristics have been extensively investigated [1–8].

It has been reported that the electrochemical performance of carbon materials is related to their crystallinity, microstructure and texture. Differences in crystallinity among carbon materials result in differences in the charge/discharge capacity and voltage profile. The graphite and highly graphitized carbons show high capacities and flat voltage curves near 0 V (versus Li/Li$^+$). The disordered carbons have a high capacity with a steep voltage profile.

The diffusion of lithium ions in the carbon materials is also an important process. The diffusion kinetics of the lithium intercalation/de-intercalation process in the carbon anode controls the rate performance and temperature characteristics of the lithium-ion cell. It is considered that the diffusivity of lithium ions in the carbon anodes is affected by the microstructure and the texture of the carbon.

The authors have developed high-capacity and high-power lithium-ion cells using graphitized mesophase-pitch-based carbon fiber (MCF) with a radial-like texture. In this study, the electrochemical characteristics of graphitized MCF were investigated as the anode of lithium-ion cells. The performance of prismatic lithium-ion cells using the graphitized MCF was also evaluated.

2. Experimental

The graphitized MCF sample was prepared at Petoca Co. Ltd. The graphitized MCF was heat-treated at 3000 °C. Fig. 1

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Fig. 1. SEM photograph of the typical cross section of the graphitized MCF.

shows the scanning electron microscopy (SEM) graph of the typical cross section of the graphitized MCF. It has a radial-like texture with a lamellar structure in the core. The average layer spacing, d_{002}, and the size of the crystalline L_c were 0.3366 and 35 nm, respectively. The average diameter of the graphitized MCF was about 8 μm and the average length of the graphitized MCF was about 20 μm. In addition to MCF heat-treated at 1000 °C, an artificial graphite (Lonza, SFG15), a natural graphite (Kansai Coke and Chemicals, NG-7) and petroleum coke were also evaluated in order to compare their electrochemical properties. The d_{002} and L_c for the artificial graphite were 0.3354 and >100 nm, respectively. The surface areas of the graphitized MCF, the artificial graphite and the natural graphite, as determined by the BET method, were 1.2, 8 and 5 m^2/g, respectively.

The electrochemical characteristics of carbon electrodes were measured using a three-electrode glass cell with a lithium counter electrode and a lithium reference electrode. Charge/discharge cycle tests were also carried out using a flat-plate sandwich-type experimental cell. The electrolyte was a 1 M $LiPF_6$/EC–DEC (ethylene carbonate–diethyl carbonate) solution.

By using the graphitized MCF anode, the $LiCoO_2$ cathode and the 1 M $LiPF_6$/EC–MEC (ethylene carbonate–methylethyl carbonate) electrolyte, 863448-size prismatic lithium-ion cells (8.6×34×48 mm) were constructed and their charge/discharge characteristics were evaluated.

3. Results and discussion

3.1. Electrochemical characteristics of carbon

The charge/discharge performance of the graphitized MCF and other carbons in the C/Li cells was evaluated from a rapid charge/discharge cycling test. Fig. 2(a) and (b) shows the discharge capacity and charge/discharge coulombic efficiency for various carbons at 2 mA/cm^2 charge and 2.5 mA/cm^2 discharge, corresponding to >0.75 C for practical lithium-ion cells. The graphitized MCF showed the highest capacity of 307 mAh/g and the highest charge/discharge coulombic efficiency. The coulombic efficiency for the graphitized MCF was 95% at the first cycle and was $>99.8\%$ after the second cycle. On the other hand, the capacity and the efficiency for graphite during the rapid charge/discharge cycling test were smaller than those of the graphitized MCF.

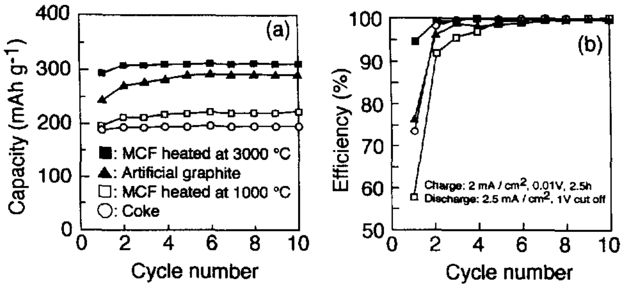

Fig. 2. Variations in (a) capacity and (b) efficiency with cycle number for various carbon anodes.

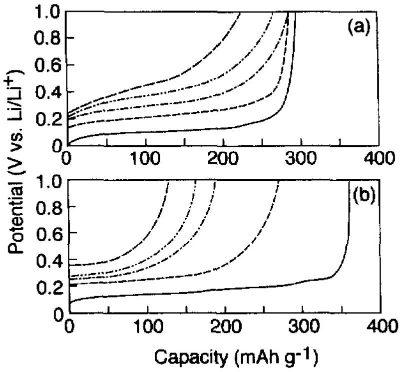

Fig. 3. Discharge curves of (a) graphitized MCF and (b) artificial graphite at various current densities: (———) 0.25 mA/cm^2; (- - -) 2.5 mA/cm^2; (– · –) 4.0 mA/cm^2; (– · · –) 5.0 mA/cm^2, and (— — —) 6.25 mA/cm^2.

Fig. 3 shows the discharge curves of the graphitized MCF anode and the artificial graphite anode at various discharge current densities [8]. While the graphitized MCF showed lower capacity than graphite at 0.25 mA/cm^2, a larger capacity was obtained at discharge rates greater than 4 mA/cm^2. The discharge capacity of the graphitized MCF at 5 mA/cm^2 showed 90% of the maximum capacity at 0.25 mA/cm^2. The capacity of graphite at 5 mA/cm^2, on the contrary, was 46% of its maximum capacity. The rate capability of the graphitized MCF anode was found to be superior to that of the artificial graphite anode.

Fig. 4 shows the variation of the chemical diffusion coefficient, D_{Li}, of lithium ions as a function of x in Li_xC_6 for graphitized MCF, natural graphite, artificial graphite, and petroleum coke at room temperature [7]. The chemical diffusion coefficient decreased almost linearly with an increase in x up to $x=0.5$. This decrease can be attributed to repulsion between lithium ions in the carbon. The values of D_{Li} for the graphitized MCF were $2\text{–}3\times10^{-7}$ cm^2/s at $x=0.1$ and $1\text{–}2\times10^{-8}$ cm^2/s at $x=0.5$, which is one order of magnitude greater than those for graphites. These results show that the graphitized MCF with a radial orientation has the advantage of rapid diffusion of lithium ions into a carbon. Diffusion into the carbon fiber can occur rapidly because the carbon fibers

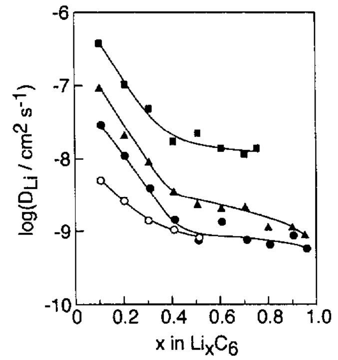

Fig. 4. Variation of chemical diffusion coefficient of lithium ions in (■) graphitized MCF; (▲) artificial graphite; (●) natural graphite and (○) petroleum coke with x in Li_xC_6 in 1 M $LiPF_6$/EC–DEC electrolyte.

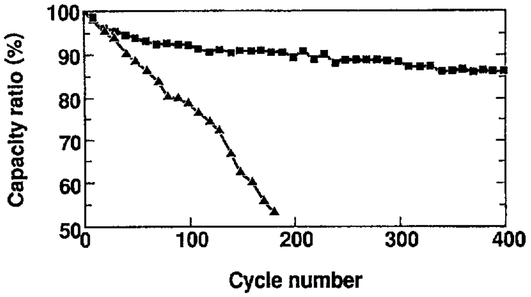

Fig. 5. Discharge capacity as a function of cycle number for flat-plate $C/LiCoO_2$ cells using: (■) graphitized MCF anode, and (▲) artificial graphite anode.

have a radial structure with a large fraction of its area accessible to lithium ions. Diffusion into graphite, on the other hand, occurs only at the narrow edge of the graphite, which may lead to slow diffusion.

Fig. 5 shows the changes in the discharge capacity with cycle number for $C/LiCoO_2$ flat-plate experimental cells using the graphitized MCF anode and the artificial graphite anode at 2 mA/cm^2 between 4.2 and 2.7 V. A long charge/discharge cycle life was obtained with the cell using graphitized MCF. The capacity ratio of the cell with the graphitized MCF anode at 400 cycles was 86% of its initial capacity. The artificial graphite anode showed poor cycling performance with fast capacity decline during cycling. The graphitized MCF may be electrochemically and chemically stable during long-term rapid charge/discharge cycling.

3.2. Performance of prismatic cells

Based on the electrochemical characteristic results in the experimental cell, the authors constructed prismatic lithium-ion cells using the graphitized MCF anode and $LiCoO_2$ cathode.

Fig. 6 shows discharge curves between 4.2 and 2.7 V for the prismatic lithium-ion cells with anodes containing graphitized MCF and petroleum coke. The cell using graphitized MCF showed 40% higher capacity (> 1 Ah) than the cell with petroleum coke, and gave a flat voltage curve. The energy density of the prismatic cell with the graphitized MCF was 270 Wh/dm^3 and 95 Wh/kg based on the total volume and weight of the cell including the case.

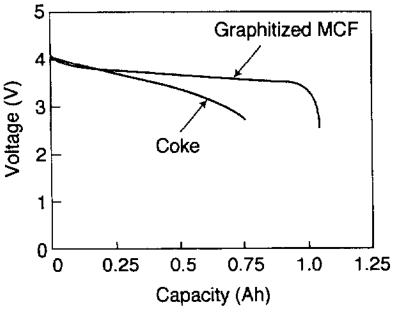

Fig. 6. Discharge curves of 863448-size prismatic cells.

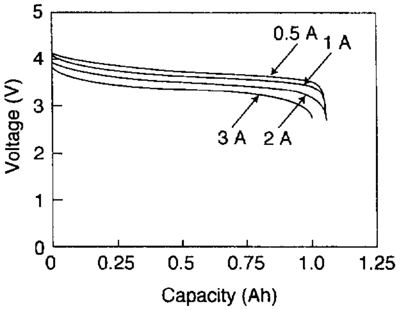

Fig. 7. Discharge curves of the 863448-size prismatic cell using the graphitized MCF with various discharge currents.

The 18650-size (18 mm in diameter and 65 mm in height) lithium-ion cylindrical cell, on the other hand, showed a high capacity of 1400 mAh, and achieved an energy density of 310 Wh/dm^3 and 120 Wh/kg.

Fig. 7 shows the discharge curves of these lithium-ion cells at various discharge currents between 4.2 and 2.7 V. The capacities below 2 A discharge were more than 1 Ah. Even at 3 A discharge, the prismatic cell had 93% of its capacity at 0.5 A discharge with a mid-discharge voltage of 3.35 V. These high-rate capabilities show that lithium-ion cells using the graphitized MCF anode provide superior rate performance compared with cells using other carbon materials. The radial-like texture and the high degree of graphitization of the graphitized MCF contribute to the rapid diffusion of lithium ions inside the carbon fiber, resulting in the high-rate performance of these lithium-ion cells.

The charge/discharge cycle life of the cell with graphitized MCF anode is shown in Fig. 8. The charge/discharge rate was 0.9 A. The cell maintained > 85% of its initial capacity

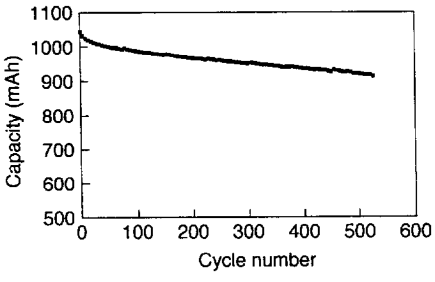

Fig. 8. Charge/discharge cycle life of the 863448-size prismatic cell using the graphitized MCF.

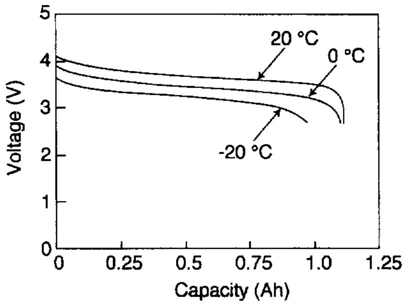

Fig. 9. Discharge curves of the 863448-size prismatic cell using the graphitized MCF at various temperatures.

after 500 cycles under this high-rate charge/discharge condition. Prismatic lithium-ion cell using graphitized MCF anode has thus been demonstrated to have good cycle life between 4.2 and 2.7 V.

The discharge performance of the prismatic lithium-ion cell as a function of temperature at 0.9 A between −20 and +20 °C was also measured. Fig. 9 shows the discharge curves at various temperatures. At 0 °C, the discharge voltage was lower than that at 20 °C, and the capacity maintained 99% of that at 20 °C. Even at −20 °C, the capacity was 87% of its capacity at 20 °C. The excellent performance at low temperatures can be attributed to the large surface area for intercalation/de-intercalation of lithium in the graphitized MCF with the radial-like texture.

The excellent high-rate performance and low-temperature characteristics make the lithium-ion cells using MCF anode highly desirable power sources for cellular phones and notebook personal computers.

4. Conclusions

The graphitized MCF (mesophase-pitch-based carbon fiber) anode exhibited larger capacities, a higher coulombic efficiency, a higher rate capability, and better reversibility than the graphite anode. The excellent performance of the graphitized MCF is ascribed to the carbon structure with the radial-like texture, the high degree of graphitization and the large fraction of surface area available for intercalation.

The 863448-size prismatic cells using the graphitized MCF showed a large capacity of > 1000 mAh, an excellent high-rate performance, and a high capacity at −20 °C. The cell also exhibited a long cycle life of more than 500 cycles.

These results lead to the conclusion that the graphitized MCFs show more promising performance than any other carbons, and is an attractive choice for the anode material in high-energy density and high-power lithium-ion cells.

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