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Short communication

Electrochemical characteristics of needle coke refined by molten caustic leaching as an anode material for a lithium-ion battery

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Abstract

Needle coke, the remaining material after refining petroleum, is used as an anode of a lithium-ion secondary battery. Sulfur is separated from the needle coke to below 0.1 wt.% using the molten caustic leaching (MCL) method developed at the Korea Institute of Energy Research. The needle coke with high-purity is carbonized at various temperatures, namely 0, 500, 700 and 900 °C. The coke treated at 700 °C gives a first and second discharge capacity of more than 560 and 460 mAh g^{-1}, respectively, between 0 and 2.0 V. By contrast, the first and second discharge capacity of untreated coke is over 420 and 340 mAh g^{-1}, respectively, between 0.05 and 2.0 V.The first discharge capacity of 560 mAh g^{-1} is beyond the theoretical maximum capacity of 372 mAh g^{-1} for LiC_6. Though the cycle efficiency is not consistent, the needle coke heat-treated at 700 °C persistently maintains an efficiency of over 90% until the 50th cycle, except on the first cycle. This study demonstrates that the needle coke with high-purity could be a good candidate for an anode material in fabricating high-capacity lithium-ion secondary batteries.

Keywords: Molten caustic leaching method; Needle coke; Sulfur; Lithium-ion secondary battery; Heat treament; Capacity

1. Introduction

Lithium-ion batteries have stimulated extensive research studies due to their high-energy storage, which enables the fabrication of smaller and lighter batteries for mobile electronics [1–3]. Non-aqueous rechargeable batteries, which use negative electrodes made from lithium containing materials than can be electrochemically intercalated and non-intercalated reversibly with lithium, are still under development in order to enhance cycle-life under deep discharge and to reduce the high reactivity of lithium metal. Therefore, investigations of new negative electrode materials are important in the development of more reliable and safer lithium rechargeable batteries. Up to the present, there have been several proposed candidate materials, among which carbon appears to be one of the most promising from the viewpoints of large specific capacity, good reversible cycling and safe operating characteristics. Various types of carbonaceous material such as graphite, carbon fibres, thermal decomposition products of polymers, pyrrole carbon and petroleum coke have been proposed for negative electrodes [4–8]. The electrochemical performance of the carbonaceous materials such as charge–discharge capacity and voltage profile is related to the crystalline structure, microstructure and texture and impurity concentration.

This study examines the electrochemical characteristics of needle coke produced from petroleum residues as an anode material for lithium-ion rechargeable batteries. The needle coke is a special grade of petroleum coke produced in delayed coking operations. Since the good quality of needle coke in terms of its structure is a main factor in enhancing the electrochemical performance, the growing method is impor-

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tant. The molten caustic leaching (MCL) method developed in the Korea Institute of Energy Research is employed here [9]. The MCL method is a chemical-refining process that can effectively cut the organic bonding between carbon and sulfur and rapidly transform constituents such as Si, Fe, V and Ni into water–salt; it is performed at a comparatively low temperature of 400–600 °C in an autoclave. The electrochemical behaviour of the needle coke with respect to the annealing temperature is investigated by means of charge–discharge cycling at constant current.

2. Experimental

Petroleum coke which is produced through the refining of crude petroleum contains appreciable amounts of sulfur, generally 6–10 wt.%. The sulfur causes swelling or bloating ('puffing') of green electrodes during graphitization. The sulfur in the petroleum coke is predominatly an organic sulfur compound, and is therefore not easily separated from the coke [10]. The MCL process can, however, remove sulfur down to 0.1 wt.% or less. The needle coke was annealed at various temperatures in a high-pressure reactor so as to produce for anode materials. The chemical composition of the refined needle coke is listed in Table 1. The coke was ball-milled to particle sizes of less than 45 μm and dried at 120 °C for 24 h. The dried cokes were categorized into four groups. To find the proper heat treatment temperature for the cokes, an analysis was conducted using a thermogravimetric analyzer (TA 2050) from ambient temperature to 1000 °C at a heating rate of 20 °C min^{-1}. The measurements were performed in nitrogen gas. Samples from the four groups were heat-treated at 0, 500, 700 or 900 °C for 1 h at a heating rate of 20 °C min^{-1}. To evaluate the electrochemical characteristics, each sample was mixed with 5 wt.% denka black to serve as a conducting material, and with 5 wt.% Teflon emulsion to serve as a binder. Thin electrodes were prepared by spreading the slurry on stainless foil by a rolling machine. The thin electrodes were cut into 1.3 cm × 1.0 cm pieces and dried in a furnace at 120 °C for 3 h. Electrochemical measurements were performed in a three-electrode system in which lithium metal was used as both the counter and the reference electrodes. The electrolyte used was 1 M $LiPF_6$ dissolved in a 50:50 vol% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cells were assembled in an argon-filled dry box. Electrochemical measurements of the cells were performed at room temperature.

Table 1
Chemical composition (wt.%) of needle coke treated by the MCL process

Ash	0.29
Carbon	70.7
Hydrogen	3.54
Nitrogen	0.13
Sulfer	0.1
Oxygen	25.24
BET ($m^2\ g^{-1}$)	880

3. Results and discussion

Thermogravimetric analysis of the high-purity petroleum coke is shown in Fig. 1. The weight of the powder rapidly decreases near 100 °C to 81%. This explains why needle coke easily absorbs moisture from the air during the MCL process. For heating up to 500 °C, the weight of the powder decreases slowly to 69%, but then decreases rapidly at higher temperatures. This can be explained as follows. The CO_x, which is produced in needle coke during the MCL process, is divided from the coke and then CO_2 gas is produced and released by reaction with O_2 [10]. Based on this result, petroleum cokes were heated at 500, 700 or to 900 °C. The XRD patterns of raw coke and cokes heat-treated at different temperatures are presented in Fig. 2. Step-scanned intensity data were generated using Cu Kα radiation at a voltage of 30 kV and a current of 20 mA. The data were gathered at room temperature over a 2θ range from 5 to 90° and a scan rate of 4° min^{-1}. Broad $d(0\,0\,2)$ peaks were observed around 25° in all samples. The intensity of the peaks increases with increase in heat treatment temperature. This indicates that heat treatment improves the crystallization of carbon [11].

The charge–discharge capacities of each heated sample were measured to find the optimum heating condition of the coke. The data for five cycles are presented in Fig. 3.

The sample treated at 700 °C delivers the highest charge capacity, whereas those treated at 0 and 500 °C show no charge capacity.

The corresponding data for discharge capacity are given in Fig. 4. The sample treated at 700 °C also delivers the highest discharge capacity. On the first cycle, the maximum discharge capacity of the sample is 560 mAh g^{-1}, which is greater than the theoretical maximum value of 372 mAh g^{-1} for LiC_6. This means that carbon materials with disordered structure have higher capacity than graphitic counter parts.

The discharge capacity and the cycle efficiency for different heat treatment temperatures are listed in Table 2. The cycle

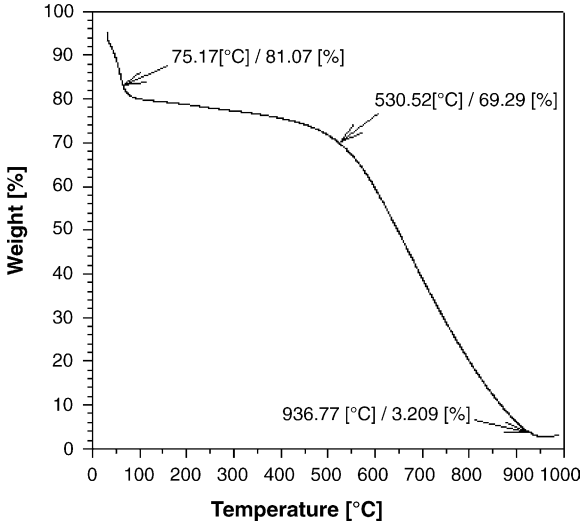

Fig. 1. TGA curves for needle coke treated by the MCL method.

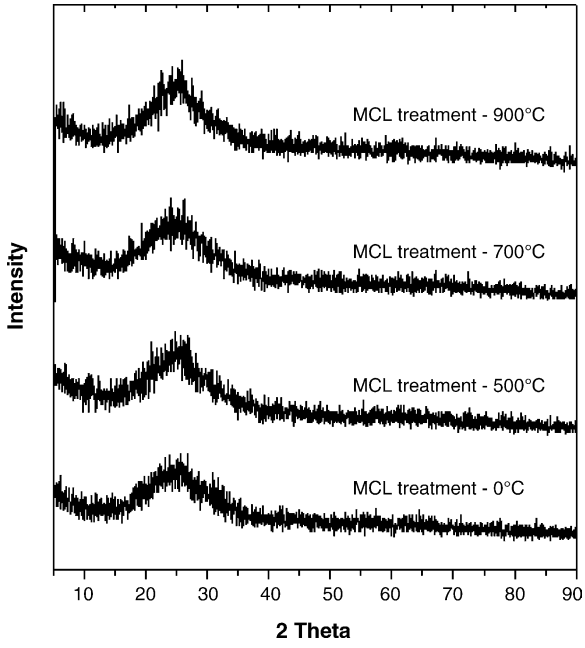

Fig. 2. XRD patterns of needle coke heat-treated at different temperatures.

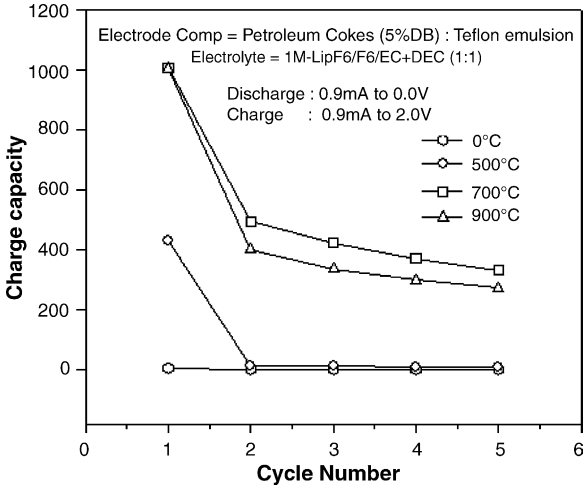

Fig. 3. Charge profile during five cycles.

efficiency is very low initially but then gradually increases. The low initial efficiency is the reason why the lithium-ions that intercalate between the carbon layers during the discharge process do not de-intercalate due to the reaction of functional groups such as –COOH, –OH, –O, $–CO_2$ and the

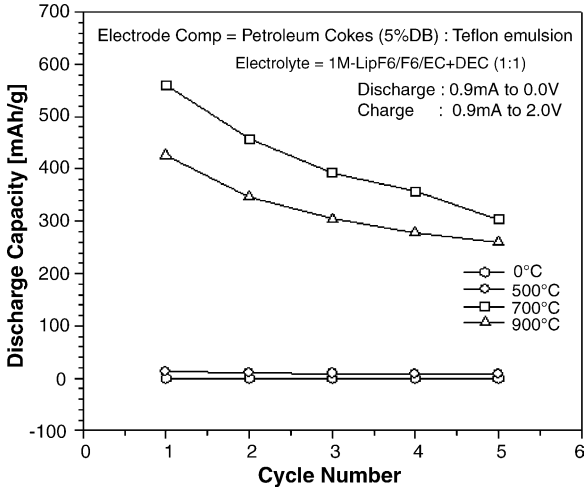

Fig. 4. Discharge profile during five cycles.

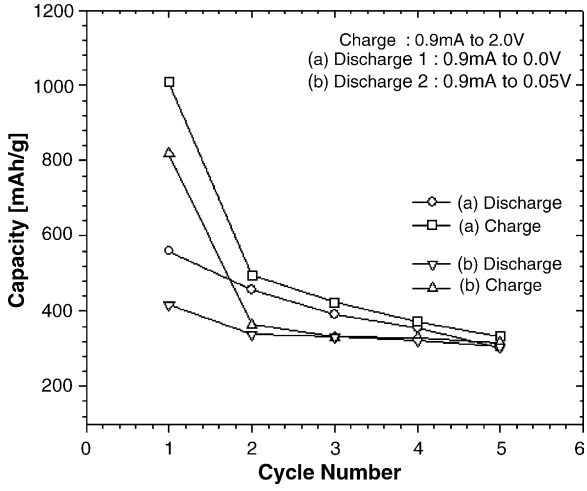

Fig. 5. Charge–discharge capacity during five cycles of needle coke heat-treated at 700 °C.

electrolyte. After the first cycle, the sample heated at 700 °C gives a cyclic efficiency of over 90% until the 50th cycle, though the cyclic efficiency is not constant. The variation in charge and discharge capacities up to the 5 cycles and the 50 cycles is showed in Figs. 5 and 6, respectively. The capacities were measured between 0 and 2 V as well as between 0.05 and 2 V. When the anode material is discharged to 0 V, the capacity is higher than discharging to 0.05 V during the fifth cycle. After the fifth cycle, however, this behaviour is reversed. A

Table 2
Initial discharge capacity and cycle efficiency for needle coke heat-treated at different temperatures

Heat (°C)	Initial discharge capacity ($mAh^3\,g^{-1}$)	Cyclic efficiency (%)							
		1	2	5	10	20	30	40	50
0	0.135	2.4	47.5	55.7	63.4	67.8	71.4	73.0	74.7
500	13.179	3.1	70.0	87.5	91.6	93.6	94.8	96.0	95.0
700	560.137	55.5	92.3	91.1	91.9	93.4	95.6	103.2	98.5
900	425.774	42.4	86.3	95.2	97.7	98.1	97.7	99.4	100.4

Electrolyte, EC–DMC + $LiPF_6$.

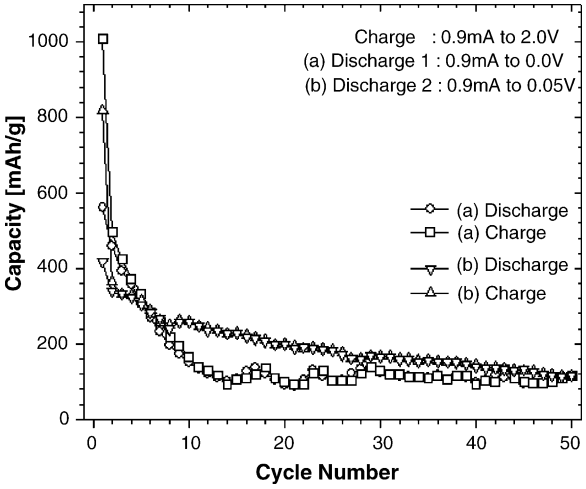

Fig. 6. Charge–discharge capacity during 50 cycles of needle coke heat-treated at 700 °C.

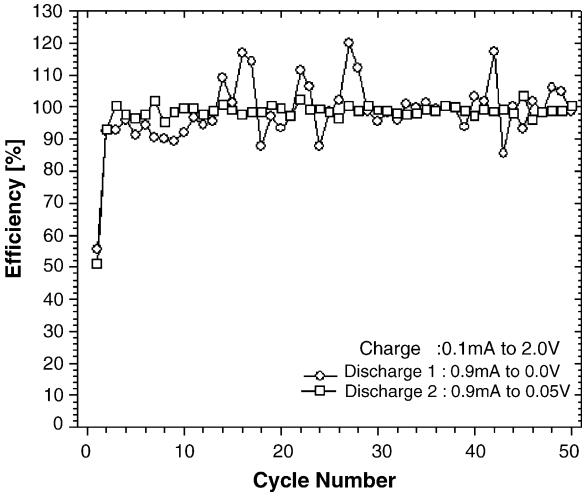

Fig. 7. Charge–discharge efficiency of needle coke heat-treated at 700 °C.

plot of efficiency versus cycle number for coke heat-treated at 700 °C is shown in Fig. 7. Stable electrochemical characteristics are observed but an irregular characteristic with a cut-off voltage of 0.05 V. This means that total discharge of the material results in destruction of the carbon structure in coke and causes a decrease in cycle efficiency.

4. Conclusions

An investigation has been made of the electrochemical characteristics of high-purity petroleum coke (sulfur refined to 0.1 wt.% by the MCL process) as anode materials for lithium-ion batteries. Increase in heat treatment temperature improves the crystallization of the carbon in the coke. The coke heat-treated at 700 °C gives a first discharge capacity of over 560 mAh g^{-1} and a second discharge capacity of 460 mAh g^{-1} when using a cut-off voltage to 0 V. By comparison, the corresponding values are over 420 and 340 mAh g^{-1} for a cut-off voltage of 0.05 V. The capacities are further lowered when the cut-off is reduced to 0 V. This study shows that high-purity needle coke is a promising candidate anode material for high-capacity lithium-ion batteries.

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