

Lithium intercalation in heat-treated petroleum cokes

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Abstract

Petroleum needle cokes were processed by air-milling and heat treatment at three temperatures, 1800, 2100 and 2350 °C, to produce a final average particle size of 10 μm. The effects of air-milling (before and after heat treatment) on the physical and microstructural properties of the petroleum coke particles were examined. The results obtained for electrochemical lithium intercalation/de-intercalation in 0.5 M LiN(CF₃SO₂)₂/EC:DMC electrolyte using these petroleum cokes after the different processing conditions are reported. © 1997 Elsevier Science S.A.

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1. Introduction

The electrochemical lithium intercalation capacity, x (in Li _{x} C₆), of carbonaceous materials varies over a range from 0 to >1 depending on the particle microstructure [1]. Carbons that are doped with other elements (e.g., phosphorus [2]) and those obtained from the low-temperature pyrolysis of organic precursors [3] can have capacities with $x > 1$ because of the lithium storage that involves mechanisms not associated with intercalation. For example, the formation of covalent lithium and lithium storage in microcavities are believed to enhance the lithium storage capabilities of some amorphous carbonaceous materials. For pure carbons, several factors affect their ability to intercalate lithium which involve the microstructure. The heat-treatment temperature is an important parameter with certain types of graphitizable cokes and carbons. The capacity in these cases can be varied significantly with carbons that are heat-treated over a broad range of temperatures. The lithium storage capacity goes through a minimum and tends to increase with increasing heat-treatment temperature of the carbon up to the temperature to form graphite (372 mAh/g or LiC₆). This trend has been observed by several groups [1,4]. We have previously reported a significant reduction (about 50%) in the performance of a carbon black (Sterling R, Cabot Corporation) that was heat-treated to 2700 °C. On the basis of transmission

electron microscopy (TEM) analysis, it was proposed that the graphitized, onion-skin-type structural orientation in the particles could limit lithium access to the internal crystallites, resulting in a reduced overall lithium capacity. A graphitized but more open structure would perhaps be more desirable for efficient lithium intercalation/de-intercalation reactions. Processing by grinding or other means to reduce the average size of the coarse particles is another important method which affects the lithium storage capacity and intercalation rate of carbonaceous materials. Tatsumi et al. [5] observed that carbon fibers that were chopped after graphitization treatment showed a significant improvement in capacity (about 1.6 times) over those that were chopped prior to graphitization.

In this work, we are examining the effects of both heat treatment and particle attrition by air-milling (either prior to or after the heat treatment) to evaluate the relative significance of these two parameters on the ability of needle petroleum cokes to intercalate lithium. These studies are focused on petroleum cokes because they are abundant and low-cost materials which are expected to be viable candidates for use in Li-ion cells.

2. Experimental

The carbonaceous materials used in this study are derived from a graphitizable calcined 'needle' petroleum coke (190LS, Superior Graphite). This coke is low in sulfur

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(< 1%) and other unwanted elements (0.05–0.15%). In this study, the coke was heat-treated in an inert atmosphere by two procedures using identical time–temperature schedules: (i) the initial petroleum coke with large particle size (–3/8" mesh ROK) was heat-treated and subsequently air-milled to a fine powder (10 μm) or (ii) the coarse petroleum coke was first air-milled to a fine powder before heat treatment. The heat treatment was conducted in a laboratory graphite-resistance tube furnace at three temperatures (1800, 2100 and 2350 $^{\circ}\text{C}$) in a flowing argon stream. A sample designation 1800 M means that the sample was first heat-treated at 1800 $^{\circ}\text{C}$ before being air-milled to the final size. Thus, the designation M1800 denotes processing in the opposite order, i.e. air-milling first.

The electrodes were prepared using a commercial carbon fiber sheet (Lydall, 0.12 mm thick) as the support matrix and carbonized phenolic resin binder. These two components account for about 10–15% of the total electrode weight. A slurry containing the carbon particles, the phenolic resin precursor (#29-217, Reichhold Chemical) and furfuryl alcohol (QO Chemicals) was spread onto the carbon fiber support and allowed to dry. The composites were then pyrolyzed in N_2 at 1050 $^{\circ}\text{C}$. The final electrode thickness was between 0.26 and 0.30 mm. Other experimental details can be found elsewhere [6].

Three cycling experiments for each carbon electrode were carried out in a 15 ml, three-electrode cylindrical cell. Lithium foils (Cyprus Foote Mineral) were used as the counter and reference electrodes. Whatman fiberglass filters (934-AH) were used as the separator between the working and counter electrodes. The electrolyte was 0.5 M trifluoromethane sulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, tradename HQ115 from 3 M) in 50:50 ethylene carbonate (EC):dimethyl carbonate (DMC) from Grant Chemical. The cells were constructed and tested at 20 ± 2 $^{\circ}\text{C}$ in a dry argon-atmosphere glove box (< 15 ppm water). The electrodes were cycled at a C/24 rate according to a procedure established earlier [6] using a Maccor battery tester. The averaged first-cycle reversible capacity and irreversible capacity of the composite electrode are obtained. Coulombic efficiency is greater than 99% and reversible capacity degrades less than 10% after four cycles.

High-resolution transmission electron microscopy (HRTEM) using a JEM-200CX and TOPCON-002B oper-

ated at 200 kV were used to examine the graphitized coke microstructure and particle morphology. The X-ray diffraction (XRD) analyses were performed using a diffractometer (Siemens Diffractometer OSP, Model D500, Germany). Detailed specimen preparation and analysis techniques were presented earlier [6]. BET surface area measurements were obtained with a multi-point method using a Micromeritics ASAP 2000 surface area analyzer. The particle size distribution was obtained from Micro-Tract analysis.

3. Results and discussion

The crystallographic properties and the electrochemical performance of the petroleum cokes are summarized in Table 1. The particle-size distributions for the petroleum cokes that are air-milled before and after heat treatment both have an average particle size near 10 μm . However, a higher maximum and a slightly narrower distribution were observed with the samples that are air-milled after heat treatment. There is a clear difference in the BET surface areas of the two sets of materials. The surface area of samples that are air-milled after heat treatment are approximately twice that of the samples air-milled prior to heat treatment (see Table 1). These results suggest that air-milling of the heat-treated petroleum cokes produces surface defects (e.g. surface cracks, fissures, etc.) that contribute additional surface area. Because the initial petroleum coke is not as hard, air-milling prior to heat treatment is not likely to introduce significant surface defects. Furthermore, subsequent heat treatment can eliminate some of the defects that may be formed. HRTEM studies showed that the lattice images of the (002) lattice planes undergo significant ordering with heat-treatment temperature. The initial sample only shows short-range ordering of the lattice planes, with increasing order obtained by progressive heat treatment. After heat treatment at 2300 $^{\circ}\text{C}$, the basal planes show long-range order indicative of graphite and the XRD analysis shows that the $d(002)$ spacing is close to the theoretical value of 3.354 \AA . XRD analyses indicate that the different sequence of air-milling and heat treatment have little influence on the crystallographic parameters L_c and L_a . This is not too surprising because the dimensions of L_c and L_a are less than 1% of the average particle diameter, and conse-

Table 1
Physical properties and electrochemical performance of petroleum coke

Sample/process condition	$d(002)$ spacing (\AA)	L_c (\AA)	Particle size (μm)	BET surface area (m^2/g)	Capacity (x in Li_xC_6)	Irreversible capacity (mAh/g)
Control, untreated	3.442	112	30-40	0.4	0.69	65
M1800, air-milling + 1800 $^{\circ}\text{C}$	3.410	436	10	5.6	0.45	81
M2100, air-milling + 2100 $^{\circ}\text{C}$	3.359	727	10	4.6	0.74	110
M2350, air-milling + 2350 $^{\circ}\text{C}$	3.358	672	10	4.3	0.81	130
1800 M, 1800 $^{\circ}\text{C}$ + air-milling	3.405	393	10	9.3	0.56	72
2100 M, 2100 $^{\circ}\text{C}$ + air-milling	3.359	538	10	9.8	0.82	70
2350 M, 2350 $^{\circ}\text{C}$ + air-milling	3.358	633	10	9.2	0.93	69

quently air-milling is not likely to affect these microstructure parameters. The noticeable change in the microstructural parameters occurs between the initial sample, which was formed at about 1200 °C, and the sample obtained by heat treatment at 1800 °C.

The potential profiles as a function of the lithium intercalation capacity, x (in Li_xC_6), for electrodes containing petroleum cokes that are air-milled prior to heat treatment are presented in Fig. 1. The corresponding results for petroleum cokes that are heat-treated before air-milling are shown in Fig. 2. In these figures, both discharge (intercalation) and charge (de-intercalation) curves are presented on the same x -axis for ease of observation and comparison. The profiles of the samples heat-treated at temperatures below 2100 °C, regardless of the milling order, show a sloping curve over the complete capacity range that is characteristic of the behavior for amorphous carbons. Flat plateaus below 0.25 V start to develop for coke that is heat-treated at higher temperatures, indicating the development of ordered graphene layers associated with the graphitic structure. The trend here is in agreement with those reported for pitch cokes [1,4].

The reversible capacity of the petroleum cokes that are heat-treated at 2350 °C is close to that obtained with natural and artificial graphites in our laboratory [6]. The irreversible capacity loss (see Table 1) associated with the formation of

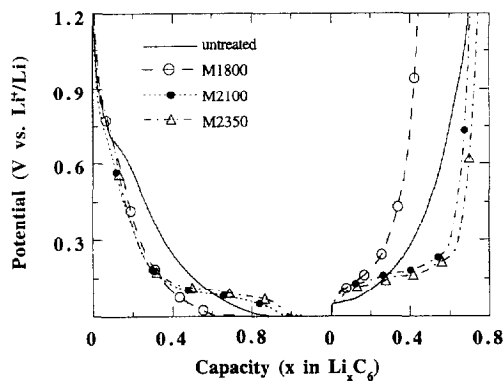


Fig. 1. Discharge and charge potential profiles as a function of capacity of the initial petroleum coke and samples that were air-milled and then heat treated at 1800, 2100 and 2350 °C.

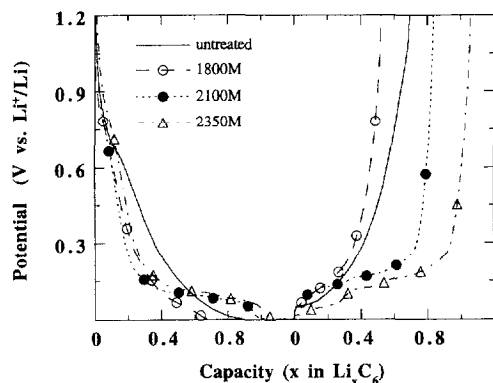


Fig. 2. Discharge and charge potential profiles as a function of capacity of the petroleum coke and samples that were heat treated at 1800, 2100 and 2350 °C before being air-milled.

the solid–electrolyte interphase does not appear to correlate with the BET surface areas as might be expected from the study by Fong et al. [7]. The irreversible capacity loss is less with the petroleum cokes that were air-milled after heat treatment. We are not yet clear about this relationship for these two series of heat-treated petroleum cokes.

The reversible lithium capacity summarized in Table 1 is plotted as a function of the $d(002)$ spacing shown in Fig. 3. There appears to be a minimum in both curves for the two series. The lowest capacity (x) of about 0.45 occurs at a $d(002)$ spacing of approximately 3.4 Å (corresponding closely to the sample heat-treated at 1800 °C). Additional data points are needed to clearly establish the minimum but the presence of one is evident. Similar results indicating the existence of a minimum in lithium capacity at a $d(002)$ spacing of about 3.44 Å with carbonaceous materials have been reported [8,9]. The significance of this minimum and the reason for its existence is outside the scope of the present discussion. However, Kinoshita and Tran [10] have speculated that it may be connected to the change in the turbostratic structure of carbons with $d(002)$ spacing near 3.44 Å.

The series of petroleum cokes that were air-milled after heat treatment clearly show a 15–20% higher capacity than those that were air-milled prior to heat treatment. It is expected that the petroleum cokes designated 1800 M, 2100 M and 2350 M contain an open structure with a large fraction of active edge-oriented surfaces that permit easier access for lithium ions and enhanced utilization of the bulk structure for intercalation. On the other hand, heat treatment of the samples after air-milling could close off certain crystallites in the bulk structure which would then not be readily accessible for lithium insertion even at a slow rate ($C/24$). The high-resolution TEM pictures show distinct changes in the microstructure, especially near the particle surface. These findings are consistent with the earlier TEM observations [6] with carbon black that was heat-treated at 2700 °C. The HRTEM results, however, suggest that the difference in particle microstructure near the surface region was not the critical factor responsible for the variation in capacity. The minimum capacity observed

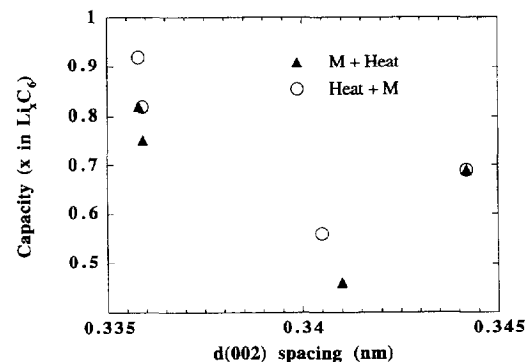


Fig. 3. Reversible capacity as a function of $d(002)$ spacing of petroleum coke obtained prior to or after heat treatment. The $d(002)$ spacing (3.442 Å) of the initial sample is denoted by its formation temperature of about 1200 °C.

is intrinsic to the carbon structure although the existence of this is not clearly understood.

4. Conclusions

The reversible lithium intercalation capacity of petroleum needle cokes is dramatically changed by the processing conditions that are used. The heat-treatment temperature is clearly important for controlling the extent of lithium intercalation. In agreement with published results, heat treatment at temperatures that produce a $d(002)$ spacing of approximately 3.4 Å are detrimental for optimizing lithium intercalation in carbonaceous materials. With the petroleum needle cokes used in this study, heat treatment to 2350 °C is sufficient to obtain a highly graphitized petroleum coke which has a reversible capacity for lithium intercalation that is close to the theoretical value for graphite.

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