

Lithium intercalation studies of petroleum cokes of different morphologies

T.D. Tran ^{a,*}, D.J. Derwin ^b, P. Zaleski ^b, X. Song ^c, K. Kinoshita ^c

^a *Chemistry and Materials Science, Lawrence Livermore National Laboratory, CA, 94550 USA*

^b *Superior Graphite, Chicago, IL 60638, USA*

^c *Energy and Environment Division, Lawrence Berkeley National Laboratory, CA, 94720 USA*

Abstract

Petroleum cokes with different morphologies are studied in lithium intercalation experiments. Several types of calcined petroleum cokes with varying microstructures and surface morphologies are heat treated at temperatures approaching 2800°C. The physical and structural properties are studied by multi-point N₂ gas adsorption analysis, particle size measurements, electron microscopies and X-ray diffraction (XRD) analysis. Changes in the properties of materials during heat treatment are significant. The effects of the coke structures and heat treatment conditions on their electrochemical lithium intercalation behavior will be discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

This work is part of our effort to identify suitable and low-cost commercial carbon anode materials for lithium-ion rechargeable batteries. Many types of carbonaceous materials have been evaluated for lithium intercalation. There are extensive data base in the literature on high-capacity carbon materials for this application (e.g., Refs. [1,2]). The carbon microstructure, size and surface morphology are generally regarded as critical for controlling the rate, lithium storage capacity and irreversible capacity. In general, materials that show high capacity (approaching that of LiC₆) and low irreversible capacity can be obtained from highly graphitized, low-surface-area carbons. The size and shape of the carbon powders are believed to play an important role in the lithium insertion/deinsertion kinetics. Granular or spherical particles with average diameters in the range of 10–20 μm have been used to facilitate Li transport [2,3]. Many of the fine and/or fractionated powders with small sizes (< 1 μm) can contribute significantly to the BET surface areas and subsequently the irreversible capacity losses. Preparation of carbon materials with these

properties can be difficult because of the heterogeneity and complexity of the carbon precursors. As part of an effort to identify suitable candidates, we have prepared these materials from calcined petroleum cokes. The availability of the cokes with various morphology and the facility with which we can control their properties can offer certain advantages. This work deals with a series of commercial petroleum cokes that have been treated thermally and physically to modify their structure and surface morphology. This is a continuation of our earlier study to investigate the effects of heat-treatment temperature and milling on the electrochemical behavior of graphitizable needle-type cokes [4,5]. Two other types of coke with different microstructural and particle morphologies are studied in this paper. The electrochemical behavior of these materials is presented and related to results from BET surface area measurements, transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD).

2. Experimental

Several types of commercial calcined petroleum coke precursors from Superior Graphite (Chicago, IL) are used as the starting materials. These are selected on the basis of their microstructural morphology and the expected final

* Corresponding author

particle morphology after air milling and partition. Three separate types of graphitizable petroleum cokes representing a wide range of morphological differences are included in this study. They are characterized as fluid coke (SO2-63-13), Santa Maria pitch coke (SO2-63-16) and LS190 needle-type coke (SO2-63-18). Fluid coke consists of spherulitic grains with a spherical layer structure that is less graphitizable. The particle morphology tends to be granular. Pitch coke is similar in morphology to fluid coke but is more easily graphitizable. In contrast, needle coke is a special type of coke with extremely high graphitizability resulting from a preferred orientation of its structure. The crystallite appears to be partially graphitized even at coking temperatures below 1400°C. The milled particles tend to assume needle-like platelets because of their structural orientation. Some TEM showed characteristic morphologies associated with these cokes. These cokes were air-milled and then sieved to between 10 and 25 μm . Their surface areas are below 10 m^2/g . All three types are commercial materials that have been (calcined) exposed to a maximum of 1400°C to remove volatile components.

The electrodes containing these powders were prepared according to a procedure which uses pyrolyzed phenolic resin as the binder [6]. The electrolyte is 0.5 M lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$; tradename HQ115, 3M) in a 50:50 mixture of ethylene carbonate and dimethyl carbonate (Grant Chemical). Intercalation experiments were done in a three-electrode cell with lithium foils as both counter and reference electrodes. Charge and discharge tests were done at $C/24$ rate. The cells were constructed and tested at $20 \pm 2^\circ\text{C}$ in a dry argon-atmosphere glove box (< 10 ppm water).

3. Results and discussion

The calcined petroleum coke precursors were milled and then sieved to indicated ranges as represented by the

average particle diameters shown in Table 1. The air milling technique minimizes the introduction of another impurity component and allows for the preparation of more granular morphologies with smooth surfaces that would yield low surface areas. The fluid coke and the Santa Maria pitch-type coke are selected because of their amorphous-like structure and their particle morphologies which are more globular in nature. In contrast, needle-like cokes such as that studied in this work (LS190) or electrode coke tend to develop platelets morphology containing large crystallites and high fraction of basal planes after graphitization and milling processes. It is expected that heat-treated materials deriving from the fluid-type and/or pitch-type cokes can lead to low surface area, graphitized and spherical-like powders more suitable for lithium insertion applications.

Table 1 shows the physicochemical data and reversible capacities of the three types of petroleum cokes. The microstructural parameters (d_{002} and L_c) were obtained from XRD analysis and they are consistent with our observations from TEM. The heat treatment resulted in graphitization of the coke microstructures as evident from the decreasing d_{002} spacing with treatment temperatures in the range between 1400 (i.e., precursor) and 2800°C. The needle-type cokes are easily graphitized as the d_{002} spacing reached 3.358 Å even only after 2-h exposure to 2300°C. This was discussed in more details earlier [5]. Crystallite growth in the direction perpendicular to the graphene layer (L_c) also increases significantly with treatment temperatures for this series. We have not been able to observe diffraction pattern from the (110) plane which would allow calculation of the in-plane layer stacking dimension (L_a). However, Raman data show some growth in the in-plane direction (L_a) as the function of heat treatment temperatures. On the other hand, the crystallite growths for fluid and pitch cokes show somewhat lesser degree of graphitization as indicated by the structural

Table 1
Physical properties and intercalation data on petroleum cokes

Sample + treatment	d_{002} (XRD) (Å)	L_c (XRD) (Å)	Particle size (μm)	BET area (m^2/g)	Capacity (x in Li_xC_6)	Irreversible capacity (mA h/g)
LS190 needle coke	3.442	112	30–40	0.4	0.69	65
Needle coke + 1800°C	3.410	436	10	5.6	0.45	81
Needle coke + 2100°C	3.359	727	10	4.6	0.74	110
Needle coke + 2350°C	3.358	672	10	4.3	0.81	130
Fluid coke	3.47	78	22	6.8	0.65	127
Fluid coke + 1800°C	3.458	128	22	2.8	0.48	82
Fluid coke + 2300°C	3.431	234	22	1.5	0.55	73
Fluid coke + 2800°C ^a	3.399		25	5.1	0.60	100
Santa Maria pitch coke	3.489	16	11	11.2	0.83	178
Pitch coke + 1800°C	3.436	168	11	4.8	0.60	100
Pitch coke + 2300°C	3.39	336	11	3.1	0.62	61
Pitch coke + 2800°C ^a	3.377		21	8.0	0.84	100

^aHT at Superior Graphite. Milling after heat treatment.

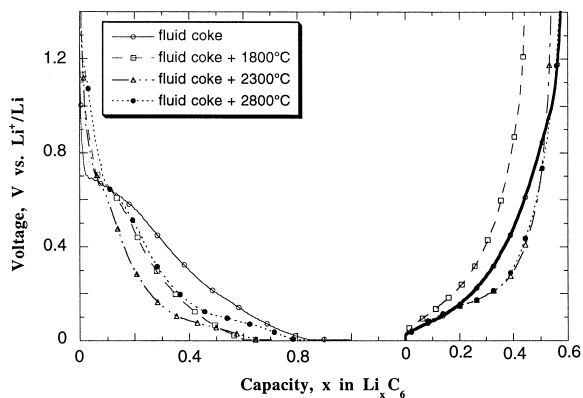


Fig. 1. Charge and discharge voltage profiles of fluid cokes at $C/24$ rate.

parameters d_{002} and L_c (see Table 1). This trend is expected on the basis of the precursor microstructure.

Fig. 1 compares the first-cycle charge/discharge profiles of fluid cokes that have been treated at different temperatures. The voltage profiles of cokes heat treated up to 2300°C still show amorphous-like behavior with gradual changes in voltage as the intercalation/deintercalation proceeds. Only the sample treated at approximately 2800°C shows the onset of graphite-like staging behavior. The total reversible lithium intercalation capacities of this fluid coke, however, remains low at about 225 mA h/g . The first-cycle intercalation/deintercalation behavior of Santa Maria pitch-type cokes treated at different temperatures is shown in Fig. 2. Similar trend can be seen with the transition from amorphous to graphitic-like staging effects occurring between 2300 and 2800°C . The flat voltage curve below 0.02 V associated with lithium intercalation in the layered graphite structure is more pronounced in this case. The total reversible lithium intercalation capacities of these treated pitch cokes are in the range of 179 to as high as 310 mA h/g , corresponding to x -values of 0.48 – 0.84 (in Li_xC_6). The highest capacities with these heat-treated cokes (at 2800°C) are about 310 mA h/g ($\text{Li}_{0.84}\text{C}_6$) which are still significantly lower than that (LiC_6) associated with

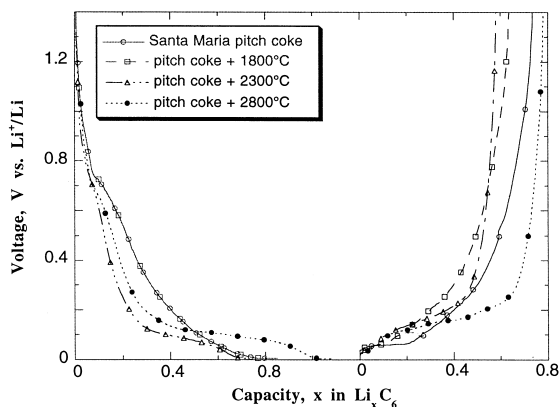


Fig. 2. Charge and discharge voltage profiles of Santa Maria pitch-type cokes.

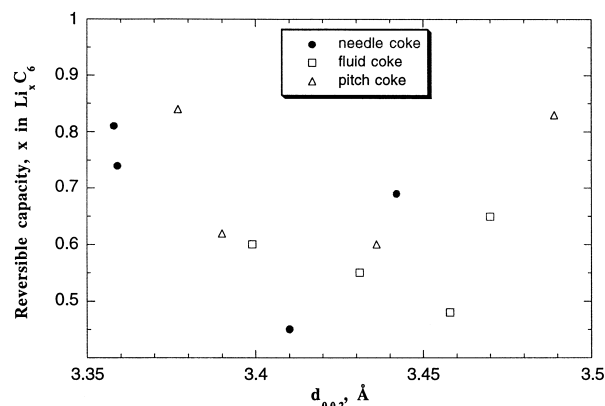


Fig. 3. Reversible capacity of heat-treated petroleum cokes as function of heat treatment temperature.

graphite. Additional heat treatment experiments are underway to investigate the effects of heat treatment protocols (i.e., time held at the maximum temperature) on the crystal microstructure and, eventually, the upper reversible capacity limits.

The average reversible capacities for all three series of heat treated cokes are shown in Fig. 3 as a function of the graphene layer spacing. The trend in the decreasing d_{002} spacing could be anticipated as the results of the increasing heat treatment temperature. The reversible capacity appears to go through a minimum over this range. This is consistent with the results on heat treated mesophase carbon microbeads (MCMB) presented by Mabuchi et al. [7]. The occurrence of the minimum appear to be different for the different type of coke and this might be a manifest of the degree of graphitization of the samples.

Successive thermal treatment of the various cokes to temperatures between 1800 and 2300°C tends to lower the BET surface areas as measured by multi-point N_2 adsorption analysis. There appears to be a corresponding reduction in the irreversible capacity losses. This trend is consistent with our general understanding of the relationship between surface area and irreversible capacity losses [8]. Discrepancies for samples of fluid and pitch cokes treated at 2800°C can be attributed to the change in the processing procedure at the manufacturer where these are milled after heat treatment. Highly-activated surfaces as the results of milling abet with non-contact air milling procedure could introduce surface species responsible for higher irreversible capacity losses. These have been observed before. A larger average particle size for these samples (treated at 2800°C) is perhaps a reflection of the harder graphitized samples prior to milling.

4. Summary

This work studies and compares three types of calcined petroleum cokes with varying microstructures and surface

morphologies that are heat treated at temperatures up to 2800°C. The physical and structural properties obtained by multi-point N₂ gas adsorption analysis, particle size measurements, electron microscopies and XRD analysis show differences in the morphologies of the particles and their microstructures. The changes in the properties of materials during heat treatment are dependent on the precursor materials and can be controlled. The reversible capacities of the materials decrease with heat treatment temperature, go through a minimum and then increase with increasing temperature. The highest reversible capacity was 310 mA h/g (Li_{0.84}C₆) for samples treated at 2800°C.

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