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LITHIUM INTERCALATION BEHAVIOR OF SURFACE-MODIFIED CARBONACEOUS MATERIALS

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The surface properties of several well-characterized commercial carbon materials were modified by thermal and chemical treatments. The reversible capacities for lithium intercalation of a sponge green coke and a fuel green coke for lithium intercalation increased by as much as 25% after heat treatment in both reducing (5% H₂/Ar) and oxidizing (CO₂) environments. The irreversible capacity loss increased significantly with CO₂ treatment at 800°C. The trend of larger capacity losses with CO₂ treatment is also observed with a synthetic graphite (SFG6) which was produced by heat treatment at about 3000°C. Carbon fibers that were first impregnated with LiOH solution followed by reaction with CO₂ to form Li₂CO₃ tended to show lower irreversible capacity losses.

INTRODUCTION

The development of carbonaceous materials for lithium intercalation covers a wide range of carbons and graphites with different properties. The carbon microstructure, physical properties and chemical composition can be tailored to a large extent to optimize its electrochemical performance such as the reversible capacity, the irreversible capacity loss and cycleability. Factors which affect these and other behavior are being studied extensively in this project. The carbon crystallographic parameters and its chemical composition (*i.e.*, surface functional groups and additives) are generally regarded as critical for obtaining a high lithium storage capacity. Many extensive works and reviews have been reported in the literature (1-6).

The irreversible capacity loss during the first cycle is attributed primarily to the formation of the solid-electrolyte interphase (SEI) (7) and associated side reactions. The SEI directly affects the carbon anode (and the cell) performance parameters such as the lithium intercalation/deintercalation capacity, cycling efficiency, charge/discharge rate, cycle life, shelf life and safety. While this phenomena at the lithium/organic electrolyte interphase have been studied extensively (7-13), the actual morphology of the SEI is regarded as complex. It is believed to change with the stage of charge and in different

electrolytes (8, 14). Peled and co-workers (8-10, 15) have discussed the SEI processes in great details. Aside from the surface area (16), factors which influence the formation of the solid-electrolyte interface (SEI) are much less understood. In widely-used EC, DEC, DMC and PC-based electrolytes, an SEI layer containing primarily Li_2CO_3 is postulated (8, 15). A number of practical means to reduce the irreversible capacity have been considered. A partial oxidation in an oxidizing atmospheres such as in the presence of acetylene black or flowing oxygen gas at elevated temperature (12) was found to improve both intercalation capacity and cycleability. The increase in performance was attributed to the increased surface area and exposed inner fiber layer but the effects on the irreversible capacity loss was not further elucidated. The removal of adsorbed water and surface hydroxyls during heat treatment in vacuum at about 1000°C was also found to increase the carbon electrochemical behavior. Peled et al. (15) reported that the addition of 1% Li_2CO_3 to a LiAsF_6 -EC/DEC electrolyte tends to increase the reversible capacity and cycleability. A mild oxidative thermal treatment ($\sim 600^\circ\text{C}$ in air) with graphites resulting in less than 6% burn-off was shown by Peled and co-workers (9) to reduce the irreversible capacity and increase the lithium intercalation capacity. Performance improvement is attributed to a strong chemically-bonded SEI at the edge-oriented (zigzag and armchair faces) surfaces and additional storage capacities at these activated sites and nanovoids. Xue and Dahn (13) have shown dramatic effects of oxidation on high capacity carbons prepared by pyrolyzing epoxy resins. Oxidation of the carbonized resins in dry air at elevated temperatures introduced oxide complexes and increased the accessibility to nanopores within the materials. The oxidative treatment caused an increase in both the irreversible capacity and the lithium storage capacity of these carbons. The removal of the surface oxides reduced a significant fraction of the irreversible capacity loss, suggesting that the oxides play an important role in the irreversible consumption of lithium.

This work examines a number of simple thermal and chemical treatments to modify the surface properties of the carbon electrodes. These changes are expected to affect the irreversible capacity loss associated with the formation of the SEI layer. The experiments are limited to several well-characterized commercial carbon materials and carbon fibers. We discuss the initial electrochemical behavior of these modified materials and available physical properties such as BET surface areas. Further experimentation and examination of the modified samples by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) are anticipated.

EXPERIMENTAL

The starting materials include sponge and fuel petroleum green cokes (Repsol Petroleo, Spain) and a synthetic graphite SFG6 (Lonza G&T, Switzerland). An activated woven carbon fiber (A10, Spectra Corp.) is also used. Table I lists the materials and their properties. The electrodes containing the carbon powders were prepared according to a procedure which uses pyrolyzed phenolic resin (No. 29-217, Reichhold Chemical) as the binder. A slurry containing the carbon powders (30-60 μm), the resin binder and furfuryl alcohol solvent was spread onto a carbon fiber support (0.12 mm thick, Lydall Corp.) and allowed to dry at room temperature. The composites were then dried at 180°C for two hours before heat treated at 1050°C for 3 hours to pyrolyze the carbon binder. The final electrodes contained approximately 90% of the carbon under study. Further details on

electrode fabrication have been reported (17). Since the fiber materials are mechanically stable, they are hand pressed into thin electrode structures and used directly in an electrochemical cell without any binder addition.

The surface modification via thermal means was accomplished by carrying the heat treatment of the carbon/resin/carbon paper composite under various gaseous environments. Experiments under a neutral (eg. N₂) or reducing (5% H₂/Ar) gaseous atmosphere were carried out at 1050°C for 3 hours. In experiments with N₂, a total weight loss of 11% was observed for fuel green coke with most of which attributable to the loss associated with phenolic resin binder pyrolysis. Under the reducing condition, the total weight losses were 12% (i.e., for fuel green coke). The treatment with an oxidizing environment was done under CO₂ gas at 800°C to minimize weight loss. The electrode weight was reduced by 8% in this case as compared to 23% when the temperature was raised to 1050°C. In these heat treatment studies, the modified electrodes were continuously exposed to the respective gaseous environment during cooling to room temperature.

Table I. List of carbon materials and their physical properties

Sample	Particle size, μm	BET area, m^2/g
Sponge green coke	30-60	1.2
Fuel green coke	30-60	3.3
SFG6 graphite	6	15.2
Activated carbon fibers, A10	10-15 (diameter)	1050

A chemical route was used to deposit Li₂CO₃ compounds on the surface of the electrodes. The carbon fibers were used directly without any treatment. Here the electrode materials were soaked in a 0.16M lithium hydroxide aqueous solution and impregnated by three successive evacuation (1 psia) and pressurization (25 psia) stages. The evacuation and pressurization steps ensure more complete impregnation into the pores and wetting of the electrode surface. The excess lithium hydroxide was then removed and the electrodes were dried at ambient conditions overnight. The impregnated electrodes were then dried under vacuum (1 psia) at 110°C for 1 hour before introduced into a jacketed 85 mm x 300 mm pressure vessel (Polaron Equipment Ltd., Watford, England). Pressurized CO₂ was continuously flushed through the vessel at a slow rate for 3 hours. The reaction was carried out at 25°C. A weight gain of approximately 1% were recorded after each successive impregnation and CO₂ reaction step. The modified electrodes were then dried at 110°C for 30 minutes before electrochemical experiments.

The electrochemical experiments were carried out in a 15 ml, three-electrode cell with a working electrode area of 1.12 cm². The counter and reference electrodes were lithium foils (Cyprus Foote Mineral). Whatman fiberglass filters (934-AH, Millipore) was used as the separator between the working and counter electrodes. The electrolyte was 0.5 M lithium trifluoromethanesulfonimide, LiN(CF₃SO₂)₂, (tradename HQ115, 3M Corp.) in a 50:50 mixture of ethylene carbonate and dimethyl carbonate (Grant Chemical). Some experiments with cokes were done in 1:10 0.5M LiAsF₆/HQ115/propylene carbonate solution. The cells were constructed and tested at 20

$\pm 2^{\circ}\text{C}$ in a dry argon-atmosphere glove box (< 5 ppm water). The charge/discharge rate is C/24 based on a LiC_6 composition. A 64-channel Maccor battery tester was used for these studies.

RESULTS AND DISCUSSION

The electrochemical performance of unmodified carbon materials for lithium intercalation is summarized in Table II. The reversible capacity is shown in terms of the fractional intercalation value x (in Li_xC_6 where x of unity corresponding to 372 mAh/g). The irreversible capacity loss (ICL) is the difference between the first cycle discharge (intercalation) and charge (deintercalation) capacities. The data show average values from two or more experiments. The x values decreased by less than 10% after the first 4 cycles and the discharge/charge current efficiency approached 100% after the second cycle in most cases.

The potential profiles are shown in Figure 1 for sponge green coke and Figure 2 for fuel green coke. Both discharge and charge curves are included where both intercalation and deintercalation x values are included on the same x -axis for convenience. The reversible capacities of sponge green coke and fuel green coke are 220 ($x = 0.59$) and 257 ($x = 0.69$) mAh/g, respectively. The electrochemical behavior and intercalation capacities are characteristics of amorphous petroleum cokes. The irreversible capacities associated with the formation of the SEI layer are 90 mAh/g for the former and 188 mAh/g for the latter coke. These results had been reported (17) and repeated many times and are used as control here. The unmodified synthetic graphite (Lonza SFG6) shows excellent behavior, having a LiC_6 composition at full capacity with a first-cycle irreversible capacity loss of 70 mAh/g. The values here are consistent with literature values for petroleum cokes and for a highly graphitic materials (18-21).

A comparison of the voltage profiles of the 5% H_2/Ar -treated coke samples and the untreated samples is shown in Figures 1 and 2. The curves reflect some improvement in the electrode performance. The reversible capacity for the modified fuel green coke, for example, increased from 257 to 442 mAh/g (x values from 0.69 to 1.19, respectively in Table II). The additional capacity occurs over the whole potential range but at a potential lower than that of the unmodified sample. The average charge (deintercalation) potential is 0.5V(vs. Li^+/Li), indicative of amorphous-type materials. A similar trend of increased reversible capacity was also observed for the modified sponge green coke. Table II summarizes these increases. The irreversible capacities of both treated samples were comparable to those of the untreated electrodes.

In the presence of H_2 at the appropriate temperature and pressure, carbon can react to form methane by the reaction (methanation reaction)

The methanation reaction was investigated by Tomita and Tamai (22) using a microbalance. They observed that active carbon started to react with hydrogen (atmospheric pressure) at temperatures as low as 800-900°C during a programmed heat

rate of 100°C/h. When the temperature reached 1050°C, the weight loss due to methanation reached 8%. We observed a weight loss of about 10% for both materials.

Table II. Electrochemical performance* of modified carbonaceous materials

Surface treatment**	Sponge coke		Fuel green coke		Synthetic graphite		Activated fibers	
	x (Li _x C ₆)	ICL, mAh/g	x (Li _x C ₆)	ICL, mAh/g	x (Li _x C ₆)	ICL, mAh/g	x (Li _x C ₆)	ICL, mAh/g
N ₂	0.59	90	0.69	188	0.96	70		
5%H ₂ /Ar	0.86	85	1.19	200	0.85	77		
CO ₂	0.80	173	0.97	215	0.86	125		
untreated							0.44	865
LiOH/ CO ₂					0.91	100	0.41	670

* ICL, irreversible capacity loss. First cycle data. Discharge/charge rate, C/24. T, 25°C.

** Treatments with N₂ and 5%H₂/Ar performed at 1050°C, with CO₂ at 800°C and with LiOH/ CO₂ at 25°C.

The methanation reaction is likely to involve the hydrogenation of C=C double bonds and the formation of C-H surface complexes. These C-H complexes have been reported and discussed by various workers (23, 24) and can explain the increase in the lithium storage capacity of the carbons. However, while the high C/H ratios in the bulk of the polymer-derived materials previous discussed (*i.e.*, ref. 24) contributed to much larger capacities (as much as 1000 mAh/g), the smaller gain here is expected to be accounted for from surface or near-surface phenomena. Surprisingly, these C-H surface complexes do not affect the irreversible electrochemical processes associated with the formation of the SEI layer (see Table II).

The methanation reactivity of a highly graphitic materials such as SFG6 graphite is expected to be lower than that of active carbons. The irreversible capacity loss is unchanged while the reduction in the lithium reversible capacity was somewhat smaller. The synthetic graphite which had been produced by graphitization at a temperature of about 3000°C appears to be stable under this condition. Previous attempts in our laboratory to influence its performance by doping this materials with phosphorous and boron under similar conditions at 1050°C did not yield advantageous results.

The reaction of carbon with CO₂ at elevated temperatures can be represented by the reaction (Boudouard reaction)

The net result is the gasification of carbon, and a concomitant weight loss. In addition, the surface area of the carbon increases as carbon is removed from the most active sites. The reaction of carbon with CO₂ has been extensively studied (25-28). This reaction involves an oxygen-transfer step

The surface complex desorbs as CO according to the reaction

where n can be 0 or >1 . For $n >1$, the number of reaction sites increases with gasification, and the surface becomes more active with burnoff. Measurements by Marsh and Taylor (29) on the CO_2 (1 atmosphere) gasification of carbonized polyfurfuryl alcohol ($400 \text{ m}^2/\text{g}$) at 620°C indicated a reaction rate of $0.01\%/h$. Data obtained by Turkdogan and Vinters (28) showed that the rate of oxidation of coconut charcoal in CO_2 (0.96 atmosphere) at 800°C was $6.6\%/h$, and the reaction rate of graphite with CO_2 was lower. Because of the high reactivity of carbon in CO_2 , the reaction temperature used in the present study was limited to 800°C . Finally it is noted that the net result of reacting CO_2 and carbon is to increase the surface area and to form an oxygen surface complex which both influence the Li intercalation performance of the carbons used in our study.

The voltage profiles of the CO_2 -treated sponge coke and fuel coke electrodes are included in Figures 1 and 2, respectively. Table II shows that the x values for these materials increase by about 25% relative to the unmodified electrodes. The gain in capacities, however, occurs near the top of the potential curves ($>0.8\text{V}$). The hysteresis is similar in both treated cokes. Peled et al. (9) as well as Xue and Dahn (13) have postulated that the oxidation treatment (abeit at different conditions) form reactive surfaces and nanovoids within the bulk of the graphite and resin-based carbons, respectively. Additional lithium storage capacities associated with these changes contributed to the increase in the reversible capacity. Similar mechanisms can explain the results. However, it is not clear to us the extent of the effects of the oxidative treatment on the bulk structure of the carbons. Additional experiments with transmission electron microscopy could elucidate these effects.

The irreversible capacity losses increased significantly with CO_2 treatment at 800°C . The trend of larger capacity losses with CO_2 treatment is also observed with a synthetic graphite (SFG6). The surface reaction is evident here while bulk reactions to form nanovoids, perhaps, is limited due to the stability of the graphitic structure. The larger irreversible capacity losses, however, contradict with the advantageous effects that Peled and co-workers (9) observed in their treated graphite electrodes which resulted in a lower irreversible capacity loss.

An alternative chemical procedure to modify the surface properties of the carbons is considered. Since a major component of the passivating layer is Li_2CO_3 , it is of interest to deposit or pre-form this component of the layer to reduce the irreversible lithium consumption during the first cycle. A simple chemical route is considered which is expected to deposit Li_2CO_3 species on the carbon surface prior to electrochemical intercalation. This was done by impregnating a solution of lithium hydroxide onto the surface of the carbon followed by drying and then reacting with CO_2 to form Li_2CO_3 . The reaction can be written as

A well-characterized material, in this case, activated carbon fibers, was considered because of its high surface area and simple surface structure. As shown in Table II, the treated carbon fibers show a significant reduction in the irreversible capacity

loss although it is still substantial because of the high surface area of the fiber. The first cycle shows a reduction from 865 to 670 mAh/g. The discharge (intercalation)/charge (deintercalation) profiles of the untreated and treated activated carbon fibers are compared in Figure 3. The effect of the treatment on the reversible capacity appear to be minimal at this point. While hysteresis can be seen for the charge and the discharge profile and the reversible capacity of the fiber is low ($x \sim 0.44$), the results serve to illustrate the preliminary advantages in using a simple modification procedure.

The chemical procedure appears to be too mild to affect the surface of the synthetic graphite which contains a large fraction of inert basal planes (30). While the LiOH/CO₂ treatments create surface species that would consume electrons during the first discharge, the by-products might not be useful nor chemically bonded to the surface to form a true passivating layer for subsequent lithium intercalation. We intend to continue this investigation with additional characterization experiments.

SUMMARY

The results indicate that the electrochemical behavior of carbons for lithium intercalation can be modified by simple thermal treatments under neutral (N₂), reducing (5%H₂) and oxidizing (CO₂), and consistent with previous work in the literature. The role of surface functional groups on the formation of the passivating film and on the reversible interaction with lithium is still a subject of investigation. The effects are complicated and additional characterization of the surface species and resulting SEI layer are critical.

A chemical procedure to deposit a component or several components of the SEI layer on the carbon surface appears to show some promise. However, the procedure in our experiments apparently only physically fills certain pores resulting in a reduction in the surface area, which leads to a lower irreversible capacity loss. For low-surface-area materials (SFG6), a more appropriate technique to deposit a thin layer consisting of useful component for SEI formation would be desirable, and is part of an on-going effort in this laboratory.

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Figure 1.

Potential profiles of untreated and modified sponge green coke. First cycle data. C/24 rate. Electrolyte is 1:10 LiAsF₆:HQ115 in PC. See experimental section for details of the thermal treatments.

Figure 2.

Potential profiles of untreated and modified fuel green coke. First cycle data. C/24 rate. Electrolyte, 1:10 LiAsF₆:HQ115 in PC. See experimental section for details of the thermal treatments.

Figure 3.

Potential profiles of untreated and chemically treated activated fibers showing a reduction in the irreversible capacity loss.

Key words

Lithium Intercalation Surface-Modified Treatment Capacity loss SEI

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