



ELSEVIER

Journal of Power Sources 54 (1995) 11–15

JOURNAL OF
**POWER
SOURCES**

Novel forms of carbon as potential anodes for lithium batteries

Randall E. Winans, Kathleen A. Carrado

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

Abstract

The objective of this study is to design and synthesize novel carbons as potential electrode materials for lithium rechargeable batteries. A synthetic approach which utilizes inorganic templates is described and initial characterization results are discussed. The templates also act as a catalyst enabling carbon formation at low temperatures. This synthetic approach should make it easier to control the surface and bulk characteristics of these carbons.

Keywords: Carbon; Anode; Rechargeable lithium batteries

1. Introduction

Electrode materials and their interfaces with electrolytes are critical areas that need to be addressed for the improvement of secondary lithium batteries. This paper will examine recent research in the development of materials for the negative electrode and will explore new approaches for preparing electrode materials.

Carbon is the material of choice for the negative electrode of these batteries [1–3]. Originally lithium metal was used for this electrode, but some severe problems ended its commercial application. First, dendrite growth on the electrode reduced its cycle life. Second, and more important, was the safety issue. These batteries tended to self-heat and sometimes ignite. Consequently, the more recent work has centered on several lithium insertion compounds that maintain a lithium activity close to unity [2], a value that is ideally suitable for a negative electrode. Graphite and other forms of carbon readily intercalate lithium metal. The exact composition of these Li_xC_6 compounds depends on the form of the carbon; for graphite, $x = 1.0$ and in some petroleum cokes, x is nearly 1.0 at room temperature. An important advantage of carbon over other host insertion compounds is that the potential is very close to that of lithium metal. A disadvantage is that the potential changes by as much as 1.5 V as the transfer of the lithium occurs [2].

The specific capacity for the negative electrode is smaller for lithium insertion compounds than for lithium metal. However, carbon electrodes appear superior in this respect to the metal oxide alternatives that have

been examined [2]. Another important consideration is the diffusion of lithium into the electrode and its influence on the rates of charge and discharge. This matter is not well understood, and needs to be studied to define the limiting processes and provide information that can be used to guide synthetic approaches. The micro-texture [2,4,5] and the surface area of the electrode material are also significant. These properties make petroleum coke a better electrode than graphite.

The changing nature of the carbon electrode surface during the first charging cycle is another important factor in overall performance. Apparently, a film is formed on the electrode surface [6]. This film protects the cathode and prevents electrolyte from being carried into the electrode, and it contains the lithium metal that is lost in the first cycle. As expected, the amount of passivating film that forms is proportional to the surface area [6]. However, only a limited range of surface areas was explored, from 1.5 to 22.5 $\text{m}^2 \text{g}^{-1}$, and very high surface area carbons were not examined. We conclude that controlling the nature of the surface of the negative electrode is a critical factor, and that a potential path toward this goal is the synthesis-by-design approach.

Other types of carbon besides graphite and petroleum coke have been examined as well. Dahn et al. [7] have incorporated boron into carbon materials. Some success was obtained with boron, but they found that nitrogen had detrimental effects. On the other hand, BC_2N material has been formed by chemical vapor deposition and claimed as potentially useful [8]. Disordered carbons such as carbon black and glassy carbons have been studied by Sleigh and von Sacken [9], who observed

increased capacity while cycling above room temperature. Fullerenes (C_{60}) have been electrochemically intercalated with lithium in a step-wise process to yield Li_xC_{60} where $x = 0.5, 2, 3, 4$ and 12 [10,11]. It is interesting to note that C_{60} contains 12 five-member rings which match the maximum number of lithium intercalated. The maximum is six (M_6C_{60}) for other metals $M = K, Rb,$ and Cs with a body-centered cubic structure [10]. However, the high cost of fullerenes prohibits their application in consumer batteries. Graphite fluorides that have been prepared at high temperature $(C_2F)_n$ and $(CF)_n$, or at room temperature $(CF_xX_y)_n$ ($X = I, Br, Cl,$ and B) are claimed to be good electrode materials, but there is little documentation in the literature to support this claim [12,13]. Carbon fibers have been examined but they are inferior to petroleum coke [14]. Recently, petroleum coke has been incorporated into a PVC film to form an electrode, but there were problems with this configuration [15].

One of our goals is to design carbon electrodes with predictable porosity and surface area. We propose a new strategy that uses inorganic templates to direct the synthesis of carbons from polymeric precursors. Tomita and co-workers [16–19] have shown that layered carbons can be produced by heating polyfurfuryl alcohol or polyacrylonitrile that have been intercalated within clays such as montmorillonite. After removal of the inorganic template by acid hydrolysis, a highly-oriented graphite thin films remains. More recently they used two faujasites, a Y-zeolite and an HY-zeolite, as templates to produce three-dimensional graphitic materials with high surface areas and relatively narrow pore diameters [20]. The surface area of these materials can be controlled by subsequent high temperature treatments. Recently, a one-dimensional array of C_{60} has been prepared in a zeolite-related aluminophosphate VDI-5 [21].

A class of templates that we are studying is the synthetic pillared clays which have been designed and prepared in our laboratory [22–24]. Natural clays have a layered structure with the galleries between the layers filled with water and exchangeable ions. Clays that have been pillared (PILC) have inorganic props between the layers. This prevents the collapse of the layers upon heat treatment. In the electrode-by-design synthesis, the organic polymer precursor is dispersed between the layers and then polymerized. Recently, a method of incorporating polymers into an inorganic layered material without using a solvent has been reported [25]. Schwarz and co-workers [26] have polymerized furfuryl alcohol within a pillared bentonite clay followed by carbonization. However, their objective was to prepare an inorganic composite material and they did not remove the inorganic matrix. Our resulting carbon will, therefore, have layers with holes due to the pillars as is depicted in Fig. 1.

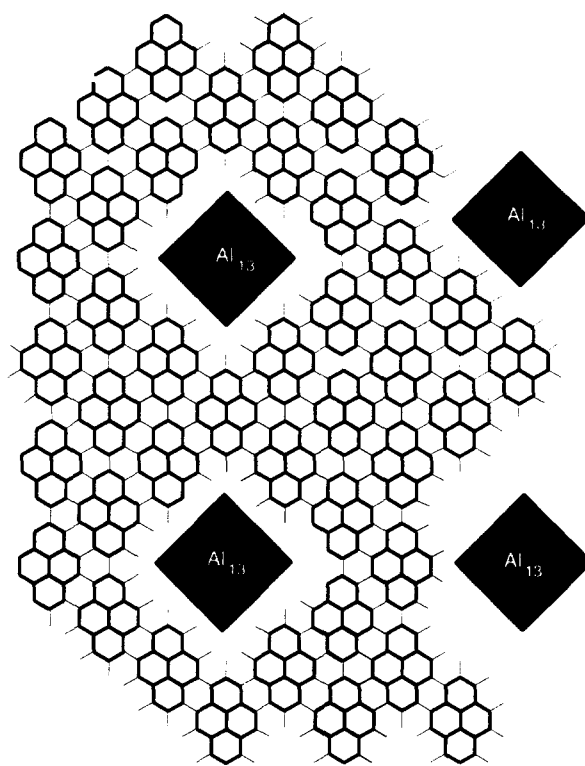


Fig. 1. A depiction of the growth of carbon sheets from pyrolysis of pyrene. The Al_{13} pillars are approximately 8 \AA square and separated on average by 14 \AA .

The extent of interlayer diffusion can be controlled by the concentration of pillars in the modified synthetic clays. Thus, the objective of our program to directly control the molecular nature of the carbons can be realized.

2. Experimental

2.1. Materials

A natural montmorillonite, Bentolite L, was used for these experiments. Detailed characterization of this clay has been published elsewhere [27]. The synthesis of pillared clays with Chlorhydrol has been previously described in detail [28]. During the preparation, the pH was kept near 5.5 by adding dilute NH_4OH . The pillared clays were calcined at $400 \text{ }^\circ\text{C}$ in air for 4 h.

Organic-loaded clays were made in the following manner. Naphthalene–montmorillonites were made by two different methods. The ‘melt’-technique heated a mixture of 1:5 naphthalene:clay at $85 \text{ }^\circ\text{C}$ in a closed container for two days. The ‘solvent’-method involved stirring the clay in a 0.5 M solution of naphthalene in benzene. The former method results in about three times more incorporation of organic by the clay. A sample of polystyrene–clay was made according to the procedure of Vaia et al. [29]. The surfactant used to

Table 1
Microanalysis of organic intercalated clay, pyrolyzed organic clay, and demineralized carbon

Sample	C (%)	H (%)
Pyrene-pillared clay	5.4	1.47
Pyrene-pillared clay, pyrolyzed	1.2	0.84
Pyrene-pillared clay, pyrolyzed and demineralized	93.8	1.86
References		
Benzene-pillared clay	0.7	1.50
Pure graphite	100.8	0.14

render the hydrophilic clay surface organophilic was a dimethyl-dialkyl quaternary ammonium chloride. Pyrene-loaded pillared clays were made by the solvent method. Typically, 6.2 g pyrene were dissolved in 300 ml benzene to which 3 g pillared clay are added, and the slurry stirred at room temperature overnight. These samples were dark green to black in color, but this color change does not occur in benzene alone or in the presence of naphthalene or polystyrene.

2.2. Pyrolysis

Most samples were pyrolyzed as reported by Sonobe et al. [30] for polyacrylonitrile–montmorillonites. In this method, the organic clays are heated at 700 °C for 3 h under N₂ flow in quartz boats.

2.3. Demineralization

The resultant carbon from the clays was liberated by standard demineralization methods, treatment by HF followed by HCl.

2.4. Characterization

Results from microanalysis are given in Table 1. X-ray powder diffraction (XRD) analyses were carried out on a Scintag PAD-V instrument using Cu K α radiation and a hyperpure germanium solid-state detector, at a scan rate of 0.25–0.5° 2 θ /min. The instrument was calibrated to the (101) reflection of low-quartz at 3.34 Å. Powders were loosely packed in horizontally held trays or spread out on glass slides. Nitrogen BET surface areas were measured on a Quantasorb Junior sorption analyzer from Quantachrome Corporation. Before measurements the samples were fully outgassed in a stream of N₂ gas; correlation of fit was 99–100%. Thermal gravimetric analysis (TGA) was performed on a Cahn 121 electrobalance from 25–800 °C at a rate of 10 °C min⁻¹ under a N₂ atmosphere. Laser desorption mass spectra (LDMS) were taken on a Kratos Maldi III using 337 nm light.

3. Results and discussion

In the XRD analysis all samples after pyrolysis and before demineralization show a peak at 3.14–3.20 Å that is not attributable to clay, and therefore must be due to an intercalated organic species, for example, see Fig. 2. After demineralization, the carbons all show a broad peak at 3.5 Å, which is about where Sonobe et al. [30] observe their peak. Sonobe attributes this peak to the (002) reflection. Dahn et al. [7] have done a thorough study on the effect of disorder in carbons on electrode properties. Based on their study, the broad (002) peak in our sample suggests that it is a highly disordered material. It would therefore have a large specific capacity if the fraction of turbostratic disorder is large and close to unity. The carbon is not highly oriented, otherwise many (001) reflections would be seen. One will notice that in some cases there is clear indication of peaks at 10.6 and 7.4 Å as well, both before and after demineralization. The 10.6 Å could be the collapsed basal spacing, indicating that minerals may still be present after demineralization. Neither peak is indicative of fluorosilicates due to incomplete HCl treatment.

Samples of pyrene/benzene–PILC and pyrene/benzene–montmorillonite were analyzed by TGA to examine thermal effects as the samples were heated in situ under N₂ flow. The results are shown in Fig. 3. The weight loss from room temperature to about 150 °C is due to water and possibly benzene. Nothing else is lost from a pure clay until about 700 °C when dehydroxylation occurs. Note that this peak is shifted

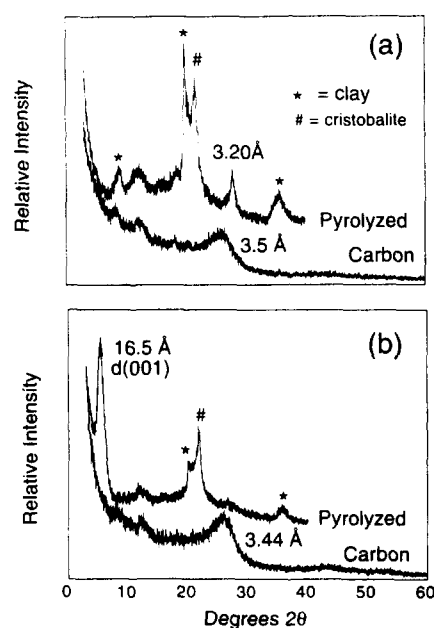


Fig. 2. X-ray powder diffraction of (a) polystyrene–montmorillonite and (b) pyrene–pillared montmorillonite systems, showing both the pyrolyzed organic clay complex and the carbon liberated after demineralization.

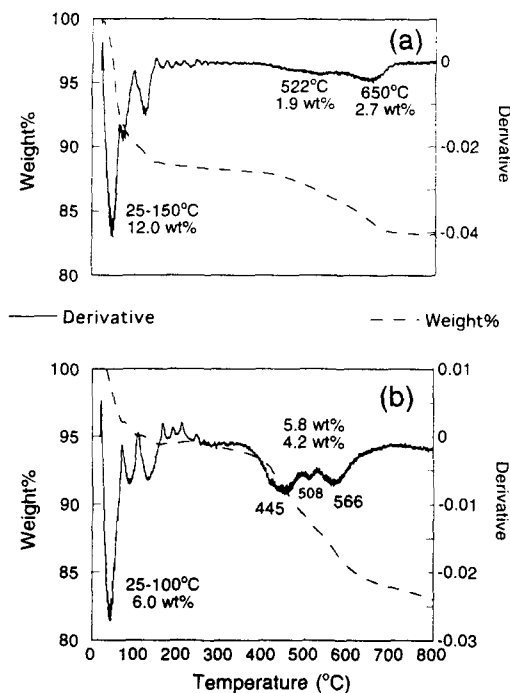


Fig. 3. Thermal gravimetric analysis under a N_2 atmosphere of (a) pyrene-montmorillonite and (b) pyrene-pillared montmorillonite; dashed curves are wt.% and solid curve is the derivative.

in the case of the organic-loaded pillared clay, to just 566 °C. Thus, pyrolyzing at 700 °C might be too high a temperature for the PILC. The weight loss regions from about 400 to about 500 °C are due to intercalated organic. Note that less than half as much is incorporated by the unpillared natural clay (on the order of 2 wt.%). The TGA value of about 5.8 wt.% liberated organic compares well with the 5.35 wt.% value obtained by microanalysis. The melting point of pyrene is 156 °C and the boiling point is 393 °C.

The surface area of the carbon from pyrene-PILC is $23 \text{ m}^2 \text{ g}^{-1}$, which compares with only $2 \text{ m}^2 \text{ g}^{-1}$ for that obtained by Sonobe. It is important to note that a fairly high surface area was produced under rather mild heating. Normally, these materials need to be heated a second time at $> 1000 \text{ °C}$ to obtain this large an area.

The LDMS spectra shown in Fig. 4 suggest that this material is highly carbonized. Even at $m/z > 1000$, the major fragments are separated by C_2 . At low mass, the fragments correspond to C_xH_y , $y = 0-3$, where the major peaks are at $y = 0$. There is no evidence for oxygen containing species which would be detrimental to the behavior of these carbons in a lithium battery. The

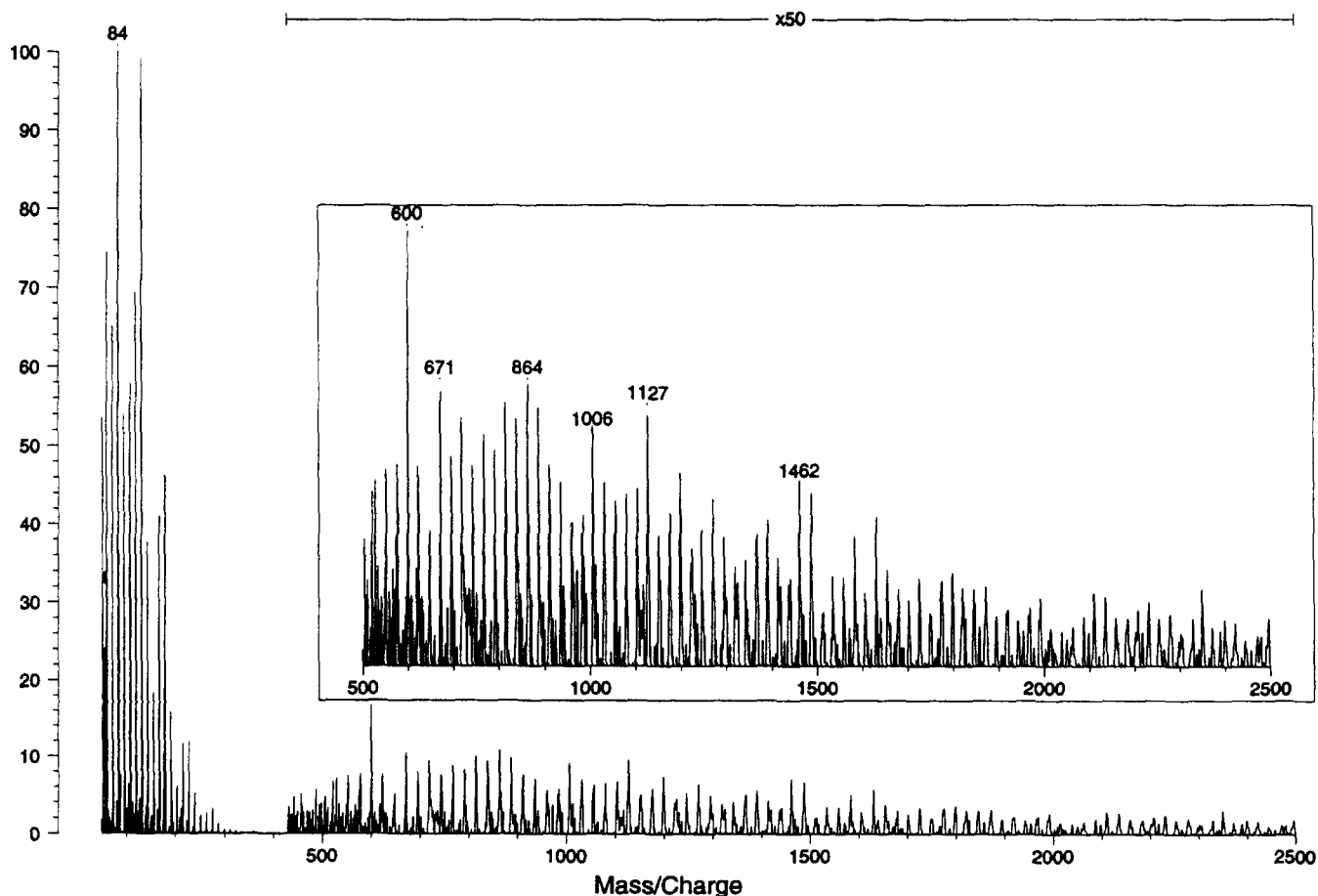


Fig. 4. Laser desorption mass spectra of demineralized pyrene-PILC (700 °C) sample at low laser power.

missing material in the elemental analysis is probably not oxygen, but could be residual inorganics.

Preliminary scanning transmission microscopy (STM) and small angle neutron scattering (SANS) data [31] strongly suggest that a layered carbon with angstrom-sized holes is produced as depicted in Fig. 1. STM results at low resolution show carbon particles the size of the clay template, and at high resolution the results suggest that there are holes in the carbon layers. Independently, SANS data indicate that 15 Å diameter holes are present, which are approximately the size of the pillaring Al₁₃ cluster. Lithium should be able to diffuse rapidly through such a molecularly porous carbon.

4. Conclusions

In summary, these approaches to carbon synthesis should yield materials with properties which can be more easily controlled than those of traditional carbons, and may, therefore, be more applicable as anodes of secondary lithium batteries. Electrochemical testing of the carbons described in this paper is being planned. In addition, milder pyrolysis conditions will be explored, and synthetic pillared clays prepared in our laboratories are going to be used as templates [22–24]. We feel that this low temperature carbonization is similar to the Scholl reaction which is acid catalyzed condensation of aromatic hydrocarbons [32].

Acknowledgements

Microanalyses were carried out by the Analytical Chemistry Division of ANL by Ms Irene Fox. The contributions of Mr J. Malinsky in obtaining TGA data and Dr J. Hunt for acquiring LDMS data is acknowledged. This work was performed under the auspices of the US Department of Energy, under contract number W-31-109-ENG-38.

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